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Mr Richard A Wheeler
Dean Academy
Franklin
Mass

Valence

H^1

Cl^1

Br^1

I^1

O^2

Cu^2_3 or 2

$Fe^?$

[illegible]

$C^{(}$

[illegible] ^{II}

SO_4^{II}

NO_3^{I}

PO_4^{III}

Mr Richard A Wheeler
Dean Academy
Franklin
Mass

[illegible]

H^1
Cl^1
Br^1
I^1
O^2
Cu^2_3 x 2
Fe
[illegible]
C
Zn^{II}

SO_4^{II}
NO_3^{I}
PO_4^{III}

$2\,HgO \rightarrow 2\,Hg + O_2$

$2\,KClO_3 \rightarrow 2\,KCl + 3O_2$

$2\,Na_2O_2 + 2H_2O \rightarrow 4\,NaOH + O_2$

M. W. LOMONOSSOV
Russian author, statesman, and chemist, 1711–1765

A TEXT-BOOK
OF
ELEMENTARY CHEMISTRY

BY

ALEXANDER SMITH

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PREFACE

In this work an attempt has been made to apply certain appropriate principles, and to do so in the thoroughgoing fashion required in an elementary treatise. One or two of these principles may be mentioned.

For example, one aim has been to provide a text suited to the needs of those who do not later continue the study of the subject. In the minds of such readers, an interest in chemistry is best awakened by calling attention to materials and processes used in the household and in commerce. A purely descriptive treatment, however, is of temporary value only. When, on the other hand, the elements of the science are presented in a somewhat rationalized form, they afford a basis for interpreting new phenomena and understanding new applications as they are met with in everyday life, and the interest in the subject is thus not only awakened, but becomes permanent and fertile. Incidental remarks showing the rôle of chemistry in the prevention of industrial waste serve to emphasize the practical value of a knowledge of the science.

Although such a course must be strictly limited in scope on the scientific side, still, so long as the foundation work is rational in method, the same plan fulfills perfectly the needs of those who afterwards continue the study of the subject. A few principles, thoroughly mastered, are better for any purpose than many principles none of which are fully grasped. In general, every book supplies the material for several different kinds of courses. The difference is created by the teacher, through the way in which he distributes the emphasis.

By making suitable omissions briefer courses can also be devised. In this way account may be taken of the maturity of the class, and of local conditions and personal preference. For example, less mature pupils, and especially those not preparing to meet some conventional requirement, can omit almost the whole of Chapter VIII, and many single sections and special explanations.

In this connection it must be kept in mind that the interests of two sexes are in part different. Thus, explosives, metallurgy, mortar, plaster, and cement are of interest especially to one sex, while plastics, starch, sugar, soap, and the nature, preparation, and digestion of foods are of special interest to the other. It is often convenient, especially during the latter half of the year, to divide the class by sexes, and to make a somewhat different selection for the two sections.

A review of what has been learned, provided it is not mere dry repetition, is many times more instructive than is the first encounter. Systematic reviewing and correlating are therefore indispensable. One effective plan is to prepare lists of questions, to which the pupils find the answers. Each list includes questions confined to the contents of a single chapter, and questions involving also important matters in previous chapters. Two varieties of such questions may be distinguished. The *first* and simpler kind of questions calls for facts or principles which can be taken directly from the text and laboratory work.* Often the class-room work may be confined to discussion and experimental illustration of the matter covered by the questions. In this way details and subjects selected for exclusion are automatically omitted. Questions of this simple sort are applicable to all pupils, mature and immature alike.

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* For example (Chap. VI): Give three examples of ways in which hydrogen may be obtained from water. Give two examples of ways of preparing it from acids. Define electrolysis, and explain how hydrogen may be liberated by its means. How can we show that hydrogen combines eagerly with oxygen? Define and illustrate reduction. Give some facts showing that the metals differ in chemical activity, *etc.*

The *second* variety of questions may involve reasoning from, and reflection upon, the facts and principles, and may not be wholly answerable by mere quotation from the text.* Such questions will powerfully stimulate the interest in the science felt by the more alert or more mature pupils. They may awaken little response from the duller or more indifferent, however, and must be used with good judgment. The exercises at the end of each chapter contain suggestions for questions, mainly of the second kind. It is assumed that the teacher will himself prefer to prepare all the simpler, systematic questions on the assigned lessons and thus give effect to his own preferences in respect to selection and emphasis.

In Chapters XXXII and XLII an opportunity for systematic review of the non-metals and of the metals, respectively, is afforded. Since it takes the form of a plan for recognizing unknown substances, the point of view is new to the pupil and even the appearance of repetition is avoided. Yet a rigorous review of a large number of facts is secured. At the same time the process invites to activity the mental traits that so successfully rivet the attention of young people upon a detective story or a guessing competition. They forget that they are learning. In performing the laboratory work connected with these chapters, the pupil makes use of the experiments previously performed, and suddenly realizes as never before some of the possibilities in the way of practical application which are characteristic of the science.

An attempt has been made to arrange the matter on pedagogical principles, though without too much distortion of the conventional order. Thus, when ozone, hydrogen peroxide, and hypochlorous acid are placed with oxygen, water, and chlorine, respectively (as they would be in a work of reference), their characteristic reactions are either omitted, or, if intro-

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* Chap. I, exercise 2. Chap. II, exercises 1, 3, 4, 5, 6, 7. Chap. III, exercises 1, 2, 3, 5, 6. Chap. IV, 1, 2, 3, 4, *etc.*

duced, prove a source of confusion to the pupil. These substances are therefore discussed together at a later stage, and no particular attention is paid to oxidation until that chapter is reached.

Again, there is danger of introducing the different kinds or categories of facts and principles in such rapid succession that mental indigestion results. The pupil should have time to become accustomed to using one set of ideas before another set is forced upon him. Hence, during the first fifteen chapters, only *matter* is considered. Heat and energy are not discussed in the chapter on oxygen, when so much that is new is undergoing assimilation, but in that on carbon (Chap. XVI), where they are equally appropriate.

The whole treatment assumes that experiments are shown in the class-room demonstrations, and that suitable laboratory work accompanies the class-room meetings.

The Author desires to thank several friends who have read the book either in manuscript or in proof and have offered valuable suggestions. He is in this respect particularly indebted to: Principal Frank L. Morse, Harrison Technical High School, Chicago; Dr. B. W. McFarland, New Haven High School; Mr. Harry A. Carpenter, West High School, Rochester; Dr. W. C. Moore, formerly of Columbia University, now research chemist with the National Carbon Co., Cleveland; Mr. P. C. Haeseler of Columbia University; and Mr. Oscar R. Flynn of the High School of Commerce (New York), who have read the whole work. He wishes also to thank Professor H. C. Sherman of Columbia University for suggestive criticism of several chapters.

ALEXANDER SMITH.

COLUMBIA UNIVERSITY,
January, 1914.

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A TEXT BOOK OF ELEMENTARY CHEMISTRY

CHAPTER I.

SUBSTANCES AND PROPERTIES.

1. When exact information in regard to any sort of material is required, we hand the material to a chemist. To learn something about the nature of chemistry, let us watch the chemist at work:

2. Properties. Suppose that the material is a piece of cloth, and we desire to know whether it is all wool, or partly cotton. The chemist places a piece of the stuff in a test-tube (Fig. 1), and pours in an amount of lye sufficient to cover it. Lye is a solution in water (98 parts) of a white solid, named by chemists, commonly, " caustic soda " and, more formally, sodium hydroxide (2 parts). The contents of the test-tube are then heated over a flame and are kept at the boiling-point for ten minutes. If the cloth dissolves entirely, leaving a clear, yellow liquid, then it was composed of nothing but wool. The chemist draws this conclusion because wool, although not affected by the boiling water, has the *property* of turning into a soluble substance when caustic soda is heated with it. If, on the other hand, the piece of cloth becomes thinner, obviously losing a part of its material, but

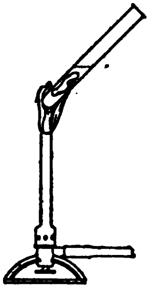
Fig. 1

leaving a part undissolved, then it contained cotton. This conclusion depends on the fact that cotton has the property of *not* being dissolved by caustic soda solution.

The same conclusion could have been reached in other ways. For example, some threads could have been taken from the edges of the sample and placed under a microscope. In this case, they would have been seen to be made up of long, hollow fibers or tubes (Fig. 2). But the cotton fibers (A) are smooth on the surface, while the woolen fibers (B) are covered with scales. By this difference in *properties*, the presence of both kinds, or of only one of the kinds, could quickly be found out. Still again, the chemist knows that wool will " take " almost any dye, while cotton remains uncolored by the greater number of dyes. He could, therefore, boil a piece of the cloth with a solution of a soluble dye — such as the red dye Ponceau 6 R, plus a little acetic acid — and then wash the sample thoroughly in clean water. On examining the cloth with a microscope he could then observe whether any fibers were still white. Here wool has the *property* of uniting with the dye, while cotton has not. The last plan could be used only with white goods, or goods not already strongly dyed.

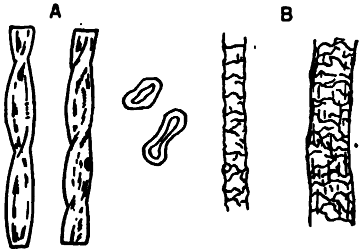

Fig. 2

The first method is the one which the chemist would probably employ in practice, because by its means he can ascertain and report, not only the presence of cotton, but the proportion of cotton present. To do this, he weighs the dry piece of cloth before placing it in the test-tube. Then, after the boiling with caustic soda solution, he washes what is left of the sample very thoroughly in running water, dries it, and weighs it again. The weight of this "residue" is that of the cotton. The difference between this and the original weight is the weight of the wool. The chemist is then able to state the percentages by weight of cotton and of wool in the original material.

3. Substances. Upon considering these operations, we can discover a *plan* which the chemist has devised and employs in his work. Different samples of cloth are of different colors and appearance, even when they contain the same proportions of cotton and wool. A general inspection is, therefore, of little value. But in certain respects *all* samples of wool are alike, such as in dissolving in caustic soda, in "taking" certain dyes and in possessing a scaly surface. Those respects in which *all* samples of wool are alike are called the *properties* of wool. Similarly *all* samples of cotton are alike in certain respects, which are called the *properties* of cotton. And the properties of cotton and of wool are different, many of them very different indeed. For the purpose of stating what he means, the chemist calls a kind of material, all specimens of which possess a certain set of properties, a *substance*. Wool is one substance,* and cotton another substance. Every *part* of a specimen of a substance has the same properties as any other part. If any portions can be found which have different properties, these are portions of another substance, accidentally or intentionally mixed with the first. The chemist calls the foreign matter an *impurity*, and the specimen an *impure* sample of the substance of which it is mainly composed.

A substance, then, is a species or kind of matter, and all specimens of it show the same set of properties. The substance is recognized by its properties.

---

* In point of fact, wool contains several substances, but they are all alike in respect to the three properties mentioned above. They differ slightly in respect to other properties, and so can be distinguished from one another.

A property such as we have in mind is more definitely called a **specific property,** or property common to all the members of a species of matter. **A specific property is a property shown by all the specimens of a given substance.**

The *plan* which the chemist uses is that of *ascertaining* whether a given material is made up of one, or of more than one substance. He then *describes* it by *naming the substances* he finds in it.

4. Another Illustration. This view-point is peculiar to the chemist. Each art or science has its own view-point — its own way of thinking about a given object. By the *geologist,* a piece of granite is at once thought of as belonging to the older rocks of the earth, and the geologist considers *when* it was formed and *how* it was formed (namely by solidification of a melted material). To the *builder,* it is a very hard stone, expensive to cut and polish, but very ornamental, and very durable. How and when it was formed does not make any difference to the builder.

To the chemist, as a *chemist,* on the other hand, the expense of cutting granite, and its ornamental character, are of no interest. Instead, the chemist notices at once that it is spotted, and, upon examining it closely, he observes that it appears to be a *mixture.* He breaks up a portion, and *studies the properties* of the fragments. Some are transparent like glass, are very hard, and in fact are in *all* respects like *quartz* or rock crystal (Fig. 3). All specimens of rock crystal, from whatever source, are alike in properties, and quartz is, therefore, a distinct substance or species of matter. Again, certain of the particles in granite are dark, and with a pen-knife can be easily split into transparent leaves, thinner than paper. These fragments are in all respects like *mica* (sheets of which, under the name of "isinglass," are used to close the windows

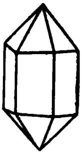

Fig. 3

of stoves), which is another substance (Fig. 4) well-known to the chemist. Still others of the fragments are less transparent than the quartz and less hard. They can be split, but with much greater difficulty than the mica. They are crystals,* oblong in shape. These are pieces of a third substance, *felspar* (Fig. 5). All the particles in the granite belong to one or other of these three kinds. The chemist, then, studies the specific properties, such as the hardnesses and the crystalline forms of various parts of the specimen and seeks to state or describe the nature of the specimen in terms of the substances he finds in it.

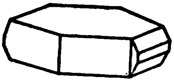

Fig. 4

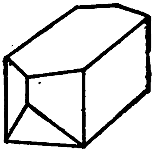

Fig. 5

5. The Law of Component Substances. That **all materials can be described in terms of certain component substances, each of which has a definite set of specific properties,** is the **first** and simplest **law of chemistry,** and at the same time the most fundamental. It was, perhaps, first clearly stated by Lomonossov (1742).

6. Mixtures. When a material contains more than one substance, it is called a **mixture.** It will be seen that the chief fact about a mixture is that **each of the component substances possesses,** while mixed with the others, **the same properties which it has when alone.** One component of a mixture does not alter any of the properties of any other component.

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* Crystals are natural forms of a geometrical nature, assumed by solid substances (§ 128).

7. Component. The **ingredients of a mixture** are called **the components** (Latin, *put with*), because they are simply placed together, without change, and can be separated without change.

8. Other Specific Properties. Beside the specific properties which happen to have occurred in these illustrations, there are others which are constantly found useful by the chemist. Thus, in the case of solids, besides the **hardness** and **crystalline form,** he gives special attention to the temperature at which the substance melts (the **melting-point**), the **specific gravity** or **density** (weight of 1 c.c., see Appendix I), the **color** and the **solubility** or non-solubility in water. In the case of liquids, the temperature at which the liquid boils under atmospheric pressure (the **boiling-point**), the **specific gravity,** the **mobility,** the **odor** and the **color** (if any) are never exactly the same for any two liquids. We shall learn more about these properties as occasions for using them arise.

9. Attributes and Conditions. It should be noted that the **mass** of a specimen is not a property, or, at least, not a specific property. Each specimen of a given substance has a different mass, although it has identical specific properties. The mass, although unchangeable, is a quality of a particular specimen only. So is it with the **volume** and the **dimensions** of a specimen. These are **attributes** of a **specimen.**

Again the **temperature** is not a property. There is no particular temperature peculiar to quartz. Even the very same specimen may be at different temperatures at different times. Temperature and **pressure** are variable and are called **conditions.** The temperature or the pressure (= state of compression) of a specimen may be changed at will. But the specific properties of a substance cannot be changed, so long as we have to do with the same substance.

10. Law of Chemical Change. When the wool was boiled with caustic soda solution, it was in some way acted upon by the caustic soda. It became soluble, and disappeared into the liquid. Wool will not dissolve in boiling water. But in the former operation its material *acquired* at least one *new* property, namely that of being soluble. Since we have defined a substance as " a species of matter, with a definite and constant set of properties," we are compelled to decide that when a piece of material *changes* its properties, it has, in doing so, become a new substance. This experiment, then, calls our attention to the **second** of the fundamental **laws of chemistry,** namely that material forming one or more substances, without ceasing to exist, **may be changed into one or more new and entirely different substances.** When such an alteration occurs, it is called a **chemical change,** or **interaction** or **reaction.** To learn more about this most mysterious fact, we shall take up in the next chapter some examples of a simple and long familiar nature.

11. Definition of Law. In science, a **law,** or **generalization** or **rule, is a statement describing some general fact or constant mode of behavior.**

12. Exercises.

1. Describe the following, by mentioning some of their specific properties: (a) water, (b) wool, (c) cotton (pp. 1–3).
2. If any of the following are mixtures, mention the facts which show them to contain more than one substance (p. 3): (a) muddy water, (b) an egg, (c) milk.
3. State and illustrate the first two laws of chemistry (pp. 5, 7).
4. Make definitions of " pure " and " impure " as applied to a sample of a substance (p. 3).
5. Give a list of the specific properties mentioned in this chapter.
6. In recognizing a specimen to be quartz, does the chemist consider (a) the weight, (b) the temperature, (c) the length of the specimen (p. 6)? If not, why not?

CHAPTER II.

Chemical Change.

13. When a piece of clean iron is lost in some damp locality such as in long grass or weeds, and is not recovered until some weeks or months have elapsed, it is found to have changed. Let us consider the change.

14. The Rusting of Metals. The outer layer of the iron has changed into a reddish crust. The red material is very brittle, it is much lighter, bulk for bulk, than iron, and it is not attracted by a magnet. These are new specific properties, for the clean iron was white, with a metallic lustre; it was tough, so that it could be bent, but not easily broken; it had nearly twice the specific gravity of the rust; and it was strongly attracted by a magnet. The new and different specific properties tell us that rust is a different substance from iron.

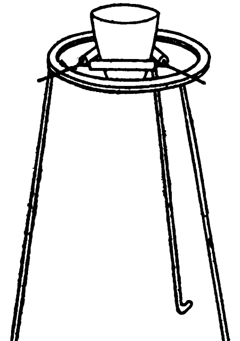

Fig. 6

It has long been known that, in a similar way, other metals can pass from a metallic to an earthy form. With the other common metals the change is slower, but it can be hastened by heating. Thus, if some tin be melted in a small, open crucible (Fig. 6), and be stirred with a piece of wire, a white powder appears on the surface. Gradually more and more of the powder is formed, and less and less of the metal remains, until, at last, all the metal is gone. Lead, when treated in the same way, gives a dirty yellowish powder.

15. Nature of Rusting. It was early observed that, although the specific gravity of the earthy product was less than that of the metal, yet there was a much greater bulk of it, and that, in fact, the earthy material weighed more than the original specimen of the metal. It seemed that, in the product, there was something besides the material of the original metal. What was the source of the additional matter, and what was its nature?

It was Lomonossov (1756) who first proved that the extra material came from the air. He placed some tin in a flask and sealed up the mouth of the vessel. The tin was heated and converted into the white powder. Upon weighing the apparatus, no change in weight was found to have occurred, but when the mouth of the flask was opened, a good deal of air rushed in, and the total weight was then greater. A portion of the original air had therefore forsaken the gaseous condition, and had joined itself with the tin to form the powder. Eighteen years later the same experiment was made and the same conclusion drawn from it by Lavoisier. The rusting of other metals was likewise found to be accompanied by increase in weight and by absorption of material from the air. Lavoisier named the gas, taken from the air, oxygen.

These conclusions can be confirmed in various ways. For example, when the air is pumped out of the flask before it is sealed, the metal can be heated in the vacuum indefinitely without rusting.

16. Chemical Combination and Compounds. When we consider these cases of rusting, we perceive that in each case a metal and a gas came together to form an earthy powder. The metal and the gas were entirely different substances, yet the product was not a mixture of these substances. It had quite different properties. Moreover, all its particles were alike, and there was only one substance in the result. Apparently, then, there are two different ways in which two (or more) substances may come together. They may form a mixture in which each substance continues to exist with its former properties, or they may come together to give a single new substance with different properties. Such a change as the latter we call a **chemical combination** or **chemical union.** The product we call a **compound substance.**

We are very careful never to speak of a compound substance as a mixture; rust is not a mixture of iron and oxygen. Nor do we ever call a mixture (like granite) a compound, or the operation of mixing, combination or union. These are technical words, in chemistry, and, to avoid confusion, may be used only with due regard to their technical meaning.

17. Constituents. As we have seen (§ 7), we speak of the substances in a mixture as the components. If we wish to refer to the materials which have combined to give the compound we call them the **constituents** (Latin, *standing together*) of the compound substances. Thus iron and oxygen are the constituents of common rust.

The name of a compound is devised so as to indicate what its constituents are. Thus iron rust is oxide of iron (or ferric oxide), the white powder from tin, oxide of tin, the product from lead, oxide of lead.

18. A Condensed Form of Statement. We may represent these changes, and indeed all chemical changes, in a condensed form, thus:

$$\text{Iron} + \text{Oxygen} \rightarrow \text{Oxide of iron (Ferric oxide).}$$

Each name stands for a substance. Two substances, in contact with one another (mixed), but not united chemically, are separated by the + sign. The arrow shows where the chemical change comes in, and the direction of the change. We read the statement thus: Iron and oxygen brought together under suitable conditions undergo chemical change into oxide of iron, called also ferric oxide. Similarly, we may write:

Tin + Oxygen → Oxide of tin.
Lead + Oxygen → Oxide of lead.

19. The Increase in Weight. As we have seen, the progress of rusting is accompanied by an increase in weight, due to the gradual addition of oxygen to the metal. It will make our ideas about rusting more definite if other facts about this increase in weight are mentioned. The increase in weight ceases of its own accord, when a certain maximum has been reached. This occurs when the last particles of the metal have disappeared. Thus, the tin gains in weight until every hundred parts of metal have gained nearly 27 parts (more exactly, 26.89 parts) of oxygen, and the lead until every hundred parts have gained a little more than 7.7 parts (or more exactly, 7.72 parts) of oxygen. At these points the metal is found to have been all used up, and prolonged heating causes no further absorption of oxygen, and no further change in the weight of the product. This fact, that each substance limits itself of its own accord to combining with a fixed proportion by weight of the other substance, in forming a given compound, is one of the most striking facts about chemical combination. In mixtures, any proportions chosen by the experimenter may be used. In chemical union the experimenter has no choice; the proportions are determined by the substances themselves. Thus 100 parts of iron, when turning into ordinary, red rust take up 43 parts of oxygen, no more or less (see Law of Definite Proportions, § 34).

20. Another Illustration. The metal zinc can be obtained in the form of a fine powder (zinc dust). If some zinc dust and some flowers of sulphur are stirred together in a mortar, the result is a mixture. Both substances are still recognizable. The zinc particles can be distinguished from the pale yellow — almost white — particles of sulphur. We can separate the components by using suitable properties. Thus sulphur, which will not dissolve in water (hot or cold), does dissolve readily in carbon disulphide. Zinc, however, does not dissolve in either of these liquids. If, therefore, part of the mixture is placed in a test-tube along with some carbon bisulphide and shaken, this liquid dissolves the sulphur and leaves the zinc. To complete the separation we must part the liquid from the zinc by filtration, and recover the sulphur by evaporation.

21. Filtration. Zinc dust, or any fine powder, mixed with a liquid or solution (like the solution of sulphur in carbon disulphide) is said to be **suspended** in the liquid. The two, the solid and the liquid, may be separated in a rough way by pouring off as much of the liquid as possible, after the solid has settled to the bottom. This is called **decantation.**

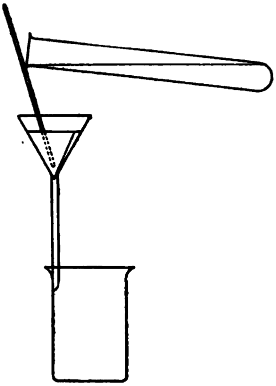

Fig. 7

A complete separation, however, can be made only by pouring the mixture on to a cone of filter paper, supported in a glass funnel (Fig. 7). The liquid, together with anything that may be dissolved in it, runs through the pores of this paper and down the stem of the funnel. The particles of the suspended solid are too large to pass through the pores, and so are found collected on the surface of the filter paper. The liquid which runs through is called the

filtrate. It will be seen that filtration, like all other operations in chemistry, takes advantage of the differing specific properties of different substances.

22. Evaporation. The liquid which runs through the filter paper is carbon disulphide containing the sulphur in solution. When this liquid is poured into an open dish, and is allowed to stand, the liquid passes off in vapor (**evaporates**). The sulphur, which gives practically no vapor at room temperatures, remains as a **residue**, in the form of crystals of rhombic outline, in the bottom of the dish (Fig. 8).

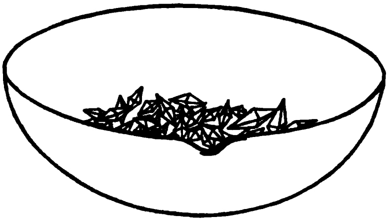

Fig. 8

The mixture of zinc dust and sulphur has thus been separated into the original zinc dust, now on the filter paper, and the original sulphur, now in the dish. The separation could be accomplished by these means, only because the material was a mixture, and not a compound.

23. Combination of Zinc and Sulphur. But zinc and sulphur are capable of combining chemically. If we alter the conditions, by raising the temperature, the chemical union takes place. To accomplish this we may place the remainder of the mixture upon a square of asbestos board, or upon a tile, and heat it by touching it with the tip of a Bunsen flame. A flash of light and a dense cloud of white smoke appear. Part of the product is in the form of the solid particles composing this cloud, the rest remains as a white powder upon the tile.

This white powder is entirely unlike both the zinc and the sulphur from which it is made. Its specific properties are different. It is white. No part of it dissolves in carbon disulphide. No parts are grey and metallic, and capable of being easily melted like zinc. It is no longer a mixture of two components. It is a single, new substance — a chemical compound formed by union of sulphur and zinc, and containing these materials as constituents.

In this connection we must not omit to notice, however, that, as in rusting (p. 11),* a certain fixed proportion of the materials will be used in forming the compound. We find that the proportion of zinc and sulphur, by weight, must be a little more than two parts of zinc to one of sulphur (more exactly, 2.04 : 1). If more zinc than this is put into the original mixture, then some zinc will be found mixed with the white product. If equal weights of zinc and sulphur are taken, then almost half the sulphur will remain uncombined. In this case, the heat given out will usually drive all the extra sulphur off as vapor.

One other point requires attention. We heated the mixture of zinc and sulphur openly, upon a board or tile. Did the air not act here, as it does in rusting? We find that these substances combine to give the same product when we heat them in a vessel from which the air had been removed. We used the tile, and ignored the presence of the air, simply to avoid the trouble of performing the experiment in a vacuum.

The metals, which, when heated in the air, combine with oxygen to give oxides, all combine also with sulphur, just as zinc does. It is only necessary to mix the metal with sulphur, and to heat the mixture. The products are called sulphides — zinc sulphide, sulphide of iron, lead sulphide, and so forth. Using the condensed statement, we may write:

Zinc (2.04) + Sulphur (1.0) → Zinc sulphide (3.04).

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* References to previous pages are used in order to save needless repetition in writing. But the beginner requires endless repetition in his reading and must *form the habit* of examining, in conjunction with the current text, the parts referred to. The passages cited are, by the reference, *made part of the current text,* which will usually not be clear without them. The same remark applies to topics referred to by name.

24. Simple and Compound Substances. By the union of two (or more) substances, we obtain compound substances. Are all substances, then, compounds? We find that some are not. We have never succeeded in obtaining iron, or tin, or lead, or sulphur, or oxygen by the simple chemical union of two or more other substances. By proper means, we can even decompose compounds, such as zinc sulphide or tin oxide, and recover the zinc and sulphur, or the tin and oxygen, as separate substances. But we have never succeeded in decomposing in this way the tin or the sulphur, the zinc or the oxygen themselves. Substances which we cannot, at will, decompose into, or make by chemical union from, other substances we call **simple** or **elementary substances,** or, more briefly, **elements.***

25. The Simple Substances or Elements. There are about eighty different simple substances, but of these the greater part are found in very small quantities, and many are of interest only to the chemist. The common materials, which are in daily use, yield, when decomposed, only about twenty different elements.

Of all the elements, only from twenty to twenty-two are known to occur in nature in their simple, uncombined condition. Three-fourths of the whole number are found in combination exclusively, and must be liberated by chemical means.

Taking the atmosphere, all terrestrial waters, and the parts of the earth's crust that have been examined, F. W. Clarke has estimated the plentifulness of the various elements. The first twelve, with the quantity of each contained in one hundred parts of terrestrial matter, are as follows:

Oxygen	49.85	Calcium	3.18	Hydrogen	0.97
Silicon	26.03	Sodium	2.33	Titanium	0.41
Aluminium	7.28	Potassium	2.33	Chlorine	0.20
Iron	4.12	Magnesium	2.11	Carbon	0.19

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* Lomonossov was probably the first to state clearly the distinction between elementary and compound substances.

Thus oxygen makes up half of the whole, and silicon (which, combined with oxygen, forms sand) one-half of the remainder.

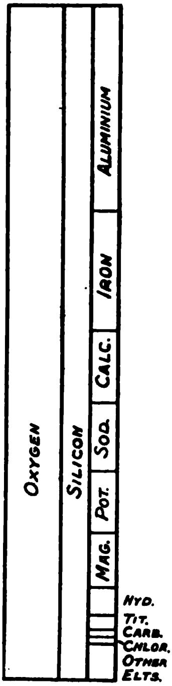

Fig. 9

Valuable and useful elementary substances that have been known from the earliest times, such as gold and silver, sulphur and mercury, are amongst the less plentiful which, all taken together, furnish the remaining 1 per cent (Fig. 9).

26. The Names of the Elements. A list of the elements will be found upon the inside of the rear cover of this book. The names which they bear are often of interesting origin. Some are named from natural compounds in which they are found, as nitrogen in nitre, aluminium in alum, potassium in potash. Some are named from places in which they were, at least at one time, obtained, as copper from Cyprus, strontium from Strontian (Argyleshire). Some are named after the country of their discoverer, as columbium, germanium, scandium, and gallium. Other names describe some property of the element, as iodine, from a Greek word for violet, and barium from the Greek word for heavy (*e.g.* *bar*ometer, iso*bar*, etc.). The names ending in *-ium* are those of metals, excepting selenium and tellurium, which are names of non-metals. Names ending in *-on* are those of non-metals, excepting iron.

27. Exercises.

1. How should you explain the fact that objects made of brass and copper slowly tarnish when exposed to the air?

2. If we stirred together sand and sugar, how should we ascertain whether the result was a compound or a mixture (§ 20)? If it proved to

be (a) a compound or (b) a mixture, should we call sand and sugar its components or its constituents (pp. 6, 10)? Is oxygen a component or a constituent of rust (§ 18)?

3. What weight of oxygen will be required to combine with 15 grams of tin (p. 11)?

4. If 5 grams of tin and 4 grams of oxygen were heated together, which of the two would remain in part unused? How much of this one would remain (p. 11)?

5. Mention some of the specific properties of: (a) the suspended material, (b) the dissolved material, (c) the liquid solvent, and of (d) the paper which are concerned in a filtration (§ 21).

6. Mention the specific properties which are used in recovering a dissolved body by evaporation of the solvent (§ 22).

7. What weight of sulphur, approximately, will be required to combine with 500 grams (see Appendix I) of zinc (p. 14)?

8. Give two ways of showing a substance to be a compound.

9. Define: Chemical union, suspension, decantation, evaporation, filtrate, residue. Give one illustration of each.

CHAPTER III.

AIR AND ITS COMPONENTS.

28. We have seen that metals absorb a gas, called oxygen, from the air, and turn into a rust or oxide. Let us now consider what happens to the air during this process.

29. The Nature of Air. Can a metal, like iron, when rusting, absorb the whole of a sample of air, or does it select a part of the air only? If we sprinkle some powdered iron in a test-tube, having first moistened the interior to cause the powder to adhere to the inside surface, and then set the tube, mouth downwards, in a dish of water (Fig. 10), we obtain before long an answer to this question. As the iron slowly removes the oxygen, the pressure of the atmosphere outside pushes the water up the tube. But, after ascending only about one-fifth of the total height of the tube, the water comes to rest. Inspection shows reddened particles where rusting has taken place, but much of the iron is still dark grey, and is as little able to rust in the remaining gas as in a vacuum. Four-fifths of the air, then, is composed of gases which do not combine with iron, and only one-fifth is oxygen. The four-fifths is in fact almost all (99 per cent) nitrogen, a substance which combines with very few materials, while the balance (1 per cent) is made up of gases which do not enter into combination with any known substances. Oxygen, on the contrary, combines with almost all simple substances, although

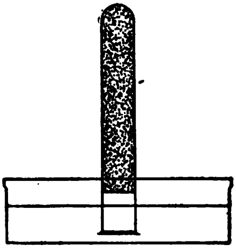

Fig. 10

in many cases, as in those of lead and tin, heating is required to hasten the process.

30. Activity and Stability. A substance which enters into combination easily is called **active,** so that oxygen is spoken of as an active element, nitrogen as a relatively **inactive** or indifferent element. An active element, since it combines greedily, naturally holds tenaciously to that with which it has combined. An active element means, therefore, also, one which is in general difficult to liberate from combination. Its compounds are in general relatively **stable.**

31. Law of the Influence of Heating. Even oxygen, active as it is, does not, visibly, combine with tin, when both are cold. Lead rusts very slowly at the ordinary temperature. Iron rusts very much faster when heated than when cold. **In every chemical change** we find that **raising the temperature hastens the process.** Other things being equal, it causes a greater quantity of material to undergo the change in a given time. This is the **third law** of chemistry.

32. Early History of Oxygen. It has long been known that air contains an active gas and an inactive gas. The Chinese recognized this fact, and called the gases *yin* and *yang*, respectively. Mayow (1643–1679) was perhaps the first to collect, by experiment, a varied knowledge of what this active gas did. He showed that it causes rusting, that it is absorbed by paint (really by the linseed oil) in drying, that it combines with combustibles like sulphur and wood, and that it supports life, being absorbed by the blood from the air entering the lungs.

There was only one thing lacking to establish the nature of oxygen, and that was the discovery of some way of obtaining a pure sample of it by liberation from a compound. But this element, because of its activity, is hard to liberate, for most of its compounds are very stable, and Mayow did not happen to discover any way of setting it free. Priestley finally (1774) obtained it by heating mercuric oxide:

Mercuric oxide → Mercury + Oxygen.

But, by that time, Mayow's work had been forgotten, and Priestley did not realize that the substance he had liberated was identical with the active component of the air. He came near to this discovery, however, for he found that a candle burned brilliantly in his gas, and a mouse lived in it.

It was Lavoisier, who had been repeating some of the earlier experiments upon the rusting of metals, and had heard of Priestley's gas from the latter's own lips, who finally saw the connection. He also proved the correctness of his idea by a conclusive experiment. He heated mercury in an enclosed volume of air and found that, as the metal slowly rusted, red particles accumulated on its surface, until one-fifth of the air was gone:

Mercury + Oxygen → Mercuric oxide.

Then he collected the rust, which was identical with Priestley's oxide of mercury, and, by heating it, recovered the oxygen and found its volume equal to that of the part of the air originally absorbed.

33. Decomposition. Priestley's experiment introduces to us a second, and very common, variety of chemical action. The first variety was combination or union (defined on p. 10). The second is called **decomposition,** and consists in taking a single substance (here mercuric oxide) and splitting it into two (or more) substances, which differ in specific properties from the substance taken, and from one another. The mercuric oxide is a red, heavy powder. The products are mercury, a liquid metal, and oxygen, a colorless gas. We have already (p. 15) noted the fact that one of the ways of showing a substance to be a compound is to use this second variety of chemical change.

34. Law of Definite Proportions. When the materials are weighed, we find that 100 parts of mercury combine with exactly 8 parts of oxygen to form mercuric oxide. Moreover, we find that every sample of mercuric oxide, whether made by combination, or made in any of the other possible ways, when decomposed, always yields mercury and oxygen in these proportions by weight. We have already seen that the oxides of tin and of lead contain fixed proportions (p. 11) of metal and oxygen, and that zinc sulphide has a definite, constant composition by weight. The same principle applies, in fact, to all chemical compounds. Any general fact is called a law, and this one, the **fourth law** that we have thus far met with, is called the **law of definite or constant proportions.** It may be stated in this form: **Every sample of any compound substance, formed or decomposed, is always found to contain the same constituent elements in the same proportions by weight.**

35. Conservation of Mass: Fifth Law. It has been shown also by innumerable experiments that when a sample of a compound is formed or decomposed, the mass of the sample of the compound is exactly equal to the sum of the masses of its chemical constituents. Experience, in fact, shows, more generally, that **the total mass of a quantity of matter is not altered by any chemical changes occurring amongst the materials composing it.**

36. Exercises.

1. Which of the metals named in Chaps. I to III appear to be most active and which least so?

2. Is mercuric oxide (p. 20) as stable as oxide of iron, or zinc sulphide? Give reasons for your answer.

3. What weight of mercury would be required to give 200 grams of mercuric oxide?

4. What methods of measuring the proportion of oxygen in air are described in this chapter?

5. In the experiment in § 29, does the weight of the powdered iron change? Does the weight of the iron and air, together, change?

6. Lavoisier heated the mercury used to extract the oxygen from the air. What law does this illustrate?

CHAPTER IV.

OXYGEN.

37. Since oxygen forms one-fifth of the atmosphere, the air of the laboratory must contain much of it. We have seen also that it tends to enter into chemical changes with a great variety of materials. Evidently, then, it is most important that we should at once learn more about it.

In the laboratory we must know in what compounds it is to be found, and with which of the substances we handle it can combine. It is perhaps even more important to know about the substances upon which oxygen has *no* chemical action. That knowledge will enable us to tell how to work without interference from the oxygen of the air, and whether we must consider oxygen as concerned in any particular chemical change we observe or not.

Outside the laboratory we expect that, upon examining the many changes which go on in nature, we shall find some of them to be of a chemical nature. In many of these cases, though not in all, we shall expect to find that the active and universally present oxygen is a factor in the change. This expectation is fulfilled, for we find that animals all require oxygen, and the higher animals take it in by breathing; that burning of coal and illuminating gas cannot go on without it; and that even many kinds of decay, which is after all a useful process, for it removes material that has become unnecessary, would cease in its absence. On the other hand, water could dry up as usual even if there were no air at all, and rain could fall even if there were no oxygen in the air.

Let us take up, then, some of the points mentioned, such as: what materials contain oxygen; how we can obtain it pure; what its specific properties as a substance are; and what it does, and what it can not do in nature and in the laboratory.

38. Occurrence. Since one-half of the material of the earth's crust is oxygen, its compounds are very common. Limestone contains 48 per cent of oxygen, sandstone over 50 per cent, and water nearly 90 per cent. The human body is about two-thirds oxygen. One-fifth (by volume) of the air is free oxygen.

39. Preparation. Unfortunately, it is difficult to liberate the oxygen from these natural substances. Niter, for example, which is found in many soils, and can be dissolved out with water, gives off oxygen when raised to a bright red heat. But it gives up, even at this temperature, only one-third of the oxygen it contains. We are driven, therefore, to employ manufactured substances.

1. *Mercuric oxide*, used by Priestley, decomposes rather easily when heated:

Mercuric oxide (108) → Mercury (100) + Oxygen (8)

The numbers in parenthesis indicate the proportions by weight. The mercury, which is liberated as vapor, condenses on the walls of the test-tube (Fig. 11), while the oxygen escapes.

2. *Potassium chlorate*, used in making matches and fireworks, is much cheaper than mercuric oxide and contains, and gives when heated, a far larger proportion of oxygen.

Potassium chlorate (100) →	Potassium chloride (61) + Oxygen (39).
Potassium	Potassium
Chlorine	Chlorine
Oxygen	

Potassium chlorate melts at 360° (Centigrade), and, as the temperature rises still higher, bubbles of oxygen appear in the liquid and break on its surface. In practice, by mixing about one part of a powdered mineral called pyrolusite (manganese dioxide) with every three parts of the potassium chlorate, we avoid using so high a temperature and secure a steadier stream of oxygen. In presence of this substance the chlorate decomposes below 200°.

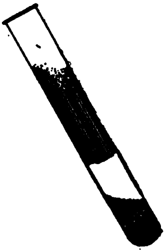
Fig. 11

The figure (Fig. 12) shows the form of apparatus commonly used. The gas passes through the delivery tube, over the end of which a bottle or jar filled with water is inverted. The gas bubbles up through the water, and collects in the bottle, allowing the water to descend into the pneumatic trough.

3. An action which yields oxygen at room temperatures, and can be started or stopped at will, is used in *oxygen generators* (Fig. 13). The latter resemble the acetylene generators used on automobiles. They work by allowing water to come in contact with lumps of **Oxone.** When sodium is burned in the air, sodium peroxide is obtained as a powder. This powder, after being melted, solidifies in the compact solid form, sold as "oxone."

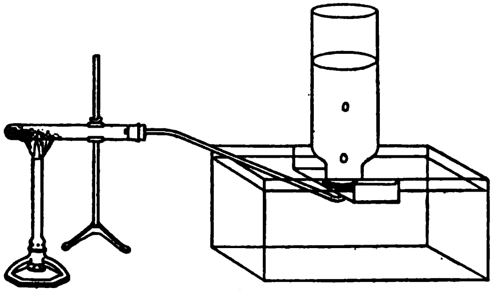
Fig. 12

Sodium peroxide +	Water →	Sodium hydroxide + Oxygen.
Sodium Oxygen	Hydrogen Oxygen	Sodium Oxygen Hydrogen

The oxone is contained in a small, sealed tin can ("cartridge"), the ends of which are perforated in several places just before use. When the valve (*B*) is opened, so that oxygen escapes, the water rises, enters the can (*C*), and interacts with the oxone. When the valve is shut, the gas drives the water down again below the level of the bottom of the can.

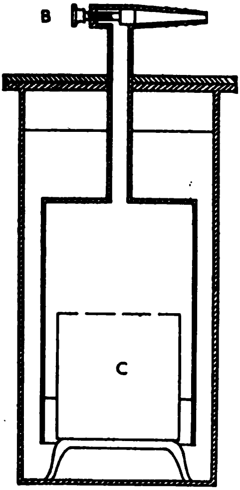

Fig. 13

4. Compressed oxygen is sold in steel cylinders (Fig. 23, p. 45). For medical purposes, 96 per cent oxygen, *made from liquefied air*, by allowing almost all the nitrogen to evaporate, is employed. With a more elaborate evaporating apparatus, pure oxygen is obtained from the same source.

40. Catalysis, or Contact Action. The influence of manganese dioxide, in causing the potassium chlorate to decompose more easily, is well worth notice. The manganese dioxide is not itself permanently altered. If the material remaining after the action is shaken with water, the potassium chloride dissolves, while the dioxide does not. Filtration (p. 12) thus enables us to recover the latter unchanged. The precise effect of the dioxide is to hasten the decomposition of the chlorate, which would otherwise be too slow at 200 degrees to be of practical value. **Substances which hasten a chemical action, without themselves undergoing any permanent change,** are called **catalytic** or **contact agents,** and the process is called **catalysis** (Greek, *decomposition*), or **contact action.** Such substances are frequently used in chemistry. Substances of this kind are secreted by animals and play a most important part in digestion and other physiological changes, enabling these changes to proceed at a rather low temperature. They have the same effect as raising the temperature (§ 31), and are especially valuable, where, as in the bodies of animals, changing the temperature is impracticable.

The oxone, mentioned above, contains a trace of cuprous hydroxide CuOH which hastens the action upon water.

41. Specific Properties are of Two Kinds, Physical and Chemical. As we have seen, every substance has an individual set of specific properties. In describing a substance it is convenient to divide these properties into two kinds. The list of other substances with which the given substance can combine chemically, for example, we place under the **specific chemical properties.** Anything the substance can do which is connected with what we consider to be a chemical change is a chemical property.

On the other hand, we do not consider melting or boiling to be chemical changes, so we place the temperatures at which the substance melts and boils, its specific gravity, and its color under **specific physical properties.**

Properties of either sort may be used for recognizing the substance.

42. Specific Physical Properties of Oxygen. Oxygen is a *colorless* gas, without *odor* or *taste.* It is a little *heavier*, bulk for bulk, than air. It can be *liquefied* by compression, provided its temperature is first brought below −118° (its critical temperature *). It *dissolves* slightly in water — 3 volumes of pure oxygen in 100 volumes of water at 20°.

This solubility of oxygen in water, although slight, is in some ways, its most important physical property. Fish secure the oxygen for their blood from that *dissolved in* the

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* The critical temperature of a gas is the temperature *below* which it must be cooled before it can be liquefied by any pressure, no matter how great.

water. In breathing animals (like man) the oxygen of the air could not be taken into the system, if it did not first dissolve in the moisture contained in the walls of the air sacs of the lungs, and then pass inwards in a dissolved state to the blood.

Liquid oxygen has a pale blue tint. In an open vessel — that is, at the pressure of one atmosphere — its boiling-point is −182.5°. When more strongly cooled, it freezes to a snow-like solid.

43. Six Specific Physical Properties of Each Gas. While every substance has a large number of physical properties, we shall consider only those which are of frequent use in chemical work. It will assist us in recalling the physical properties of a *gas*, in particular, if we remember that only *six* such properties are usually mentioned: (1) color, (2) taste, (3) odor, (4) density, (5) liquefiability (whether it is easy or difficult — with oxygen it is difficult), defined by the critical temperature, and (6) solubility (usually, in water only).

44. Specific Chemical Properties of Oxygen. We expect the chemical properties of pure oxygen to be like those of air, only more pronounced. In air iron rusts slowly when cold, and combines with the oxygen less slowly when red hot. In oxygen a bundle of picture wire or a watch spring, if once started by being heated at one end, will burn fiercely and completely, throwing off sparkling globules of the oxide,* melted by the heat.

Metals. All the familiar metals, excepting silver, gold and platinum, combine, when heated, with oxygen to give oxides, and many of them do so as vigorously as does iron.

Non-metallic Elements. Sulphur burns in oxygen with a blue flame, giving a gaseous oxide (sulphur dioxide) with a well-known odor. Phosphorus blazes very energetically

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* This is the black, magnetic oxide of iron, not identical with rus (which is red).

giving a white powdery oxide (phosphorus pentoxide). Carbon (charcoal or hard coal) glows brilliantly and is rapidly consumed, leaving an invisible, odorless gas (carbon dioxide). The proportions by weight are definite in each case: sulphur to oxygen 1 : 1, phosphorus to oxygen 31 : 40, carbon to oxygen 3 : 8.

$$\text{Carbon (3)} + \text{Oxygen (8)} \rightarrow \text{Carbon dioxide (11)}$$

Compound substances, made up largely or entirely of elements which combine with oxygen, are naturally able themselves to combine with oxygen. As a rule they give a mixture of the same oxides which each element, separately, would produce. Thus, carbon disulphide burns to give carbon dioxide and sulphur dioxide; zinc sulphide gives zinc oxide and sulphur dioxide; wood, which is composed of carbon, hydrogen, and some oxygen, gives carbon dioxide and water.

Oxygen, when pure (not mixed with other gases), is *recognized* by the fact that a splinter of wood, glowing at one end, bursts into flame when plunged into the gas.

45. Combustion and Oxidation. Rapid union with oxygen, accompanied by flames or other evidence of a high temperature, is called **combustion.** Slower union with oxygen, such as we observed in rusting metals, is called **oxidation.** We shall see later, however, that it has been found convenient to include other kinds of chemical action under the latter word, which, in consequence, has become a very useful one in chemistry.

Sometimes a mere oxidation develops into a combustion, which is then known as **spontaneous combustion.** To understand this, we must note that a given weight of material, say, iron, in combining with oxygen to form a certain oxide, will give out the same total amount of heat whether the union proceeds rapidly or slowly. If the union proceeds slowly, and the heat diffuses away, little rise in temperature will be noticed. But if the material is a poor conductor of heat, the latter will accumulate until a high temperature is reached and combustion sets in. Such a situation often arises when rags saturated with the oils used in making paint (linseed oil and turpentine) are left lying about, instead of being placed in a closed metal can, or, better still, at once burned. These oils, in "drying," combine with oxygen from the air, and turn into a tough resin-like material. Rags being poor conductors, the heat developed finally sets the mass on fire. Fires in coal bunkers arise from the same cause — slow oxidation, with accumulation of the resulting heat.

46. Uses of Oxygen. We have already mentioned several of the most important of these. The oxygen of the air, taken into the body by breathing, and carried by the blood to every part of the tissues, is used to oxidize the foodstuffs which have been absorbed during digestion. The material products are carbon dioxide and water, but the important product is the heat given out which keeps the body warm. Oxygen, compressed in steel cylinders, is used when breathing is enfeebled or stops, as in pneumonia and asphyxiation, and to renew the supply in submarine boats.

The oxygen dissolved in the water of rivers oxidizes the organic matter in the sewage discharged into them. Where the sewage enters, the water is filled with bacteria and other organisms, many of them capable, if swallowed, of producing disease. But, if there is a good flow of river water, the organic matter is oxidized, the bacteria rapidly disappear and, a few miles further down the stream, the water becomes as suitable for drinking as it was before the sewage entered.

This removal of organic matter from sewage is, in part at least, a process of decay. Decay is in large part slow oxidation promoted by bacteria and other organisms. It takes place also in animal or vegetable matter on land. It proceeds, however, as a rule, only when the material is moist. Dried fruits, dried leaves, and dried meat, whether dried by the sun or artificially, decay very slowly. When they are transferred to a moist atmosphere, bacteria and moulds begin to grow and multiply in them, and decay sets in. We can tell that decay is a chemical process, because substances with different properties, and chiefly carbon dioxide and water, are produced.

47. Substances Indifferent to Oxygen. In view of the presence of oxygen everywhere, substances which do *not* oxidize, and, when heated, do *not* burn, have many uses. Amongst the metals, silver, platinum, and gold are of this kind, and are used for ornaments. Although iron burns in pure oxygen, it oxidizes very slowly in air, even when heated, and hence can be employed in constructing fireproof buildings.

Compounds, already fully oxidized, are naturally not combustible. Of this nature are water, sand (sandstone), limestone, granite, brick, porcelain, and glass. All of these are, therefore, fireproof. Moreover they are such stable compounds that, when heated, they give up no free oxygen (water gives a very little). Glass and porcelain thus neither lose nor gain in weight when heated, and are suitable materials for chemical apparatus.

48. Exercises.

1. One hundred parts of potassium chlorate always give 39 parts of oxygen (p. 24). What law is here illustrated?
2. Why does a good draft make a fire burn more rapidly?
3. Why does a naked flame sometimes cause an explosion in a mine when the air of the mine is filled with coal dust?
4. What is the purpose of each of the things used in laying a coal fire?

CHAPTER V.

THE MEASUREMENT OF GASES. THE MOLECULAR HYPOTHESIS.

49. After the discussion in regard to the proportion of oxygen in the air and the measurement of the volume of oxygen removed (Fig. 10, p. 18), it will readily be imagined that measuring the volume of a sample of gas is a common operation in chemistry. Indeed, it is much easier to measure quantities of gas by noting their volumes than by weighing them. Some facts have to be taken account of, however, in order that the measurements of the volume may be of value.

A sample of gas diminishes in volume when the pressure increases, and it increases in volume when the temperature rises. Hence, when the volume of the gas is measured, the pressure and the temperature must also be stated.

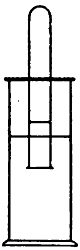

Fig. 14

50. Measurement of Pressure. In order that the pressure may be easily measured, we arrange the sample of gas so that its pressure is the same as that of the atmosphere at the moment. To do this, if, for example, the gas is contained in the narrow tube (Fig. 14), we bring the water inside the tube to the same level as that outside by lowering the tube. Then we read the volume by means of the graduation (not shown) on the tube and at the same time we read the height of the barometer.

51. Correction of the Volume to 760 mm. Pressure. Since the barometer varies in height, and the volume of a sample of gas therefore varies also, it is convenient to "correct" the volume by "reducing" it to that which the gas would occupy at "standard" pressure, namely 760 mm. Now, **the volume of a sample of gas varies inversely with the pressure (Boyle's law).** If, for example, the volume is 23 c.c. and the observed pressure of the barometer is 745 mm., Boyle's law enables us to calculate the volume the same sample of gas would occupy at 760 mm. The volume changes in the ratio of these two pressures. If the pressure of the gas were actually changed to 760 mm.,—a greater pressure—the gas would assume a smaller volume. Hence, the new volume = $23 \times \frac{745}{760} = 22.5$ c.c. That is to say, if the new volume is to be *less*, we place the *smaller pressure in the numerator.*

If a sample of gas occupies 150 c.c. at 850 mm., what volume will it occupy at 500 mm.? Here the new pressure is smaller, and the new volume therefore greater. New volume $= 150 \times \frac{850}{500} = 255$ c.c.

52. Correction of the Volume to 0° C. All gases at 0° are found to gain 1/273 of their volume when heated 1 degree, 2/273 for 2 degrees and 273/273 for 273 degrees. Thus at 273° the volume is doubled. When cooled below 0°, every gas similarly loses 1/273 of its volume for each degree. At −273°, if the regular contraction continued so far, the sample would, by calculation, at least, lose all its volume. In point of fact, however, all gases liquefy before the temperature has fallen to −273°.

The rule contained in these statements is known as **Charles' law.** By applying an arithmetical device, we can state the law in a form which makes its use in calculations quite easy. The device consists in *adding 273 algebraically to all temperatures.* The temperature, when 273 has been added, is called the **absolute temperature.** The rule then reads: **The volume of a sample of any gas is directly proportional to the absolute temperature.**

Thus, a sample of gas occupies 45 c.c. at 15°, what would be its volume at 10°? After we have applied the device, this reads: a sample of gas occupies 45 c.c. at $15 + 273 = 288°$ Abs., what would be its volume at $10 + 273 = 283°$ Abs.? The volume changes in the ratio of these absolute temperatures. Since the new temperature (10° C. or 283° Abs.) is lower, the volume becomes smaller. Therefore, putting the smaller number in the numerator, the volume at 283° = $45 \times \frac{283}{288} = 44.2$ c.c.

Again, a sample of gas occupies 125 c.c. at 25°, what will be its volume at −15°? The absolute temperatures are $25 + 273 = 298°$ Abs., and $-15 + 273 = 258°$ Abs. As the new temperature is lower, the volume will be less. Hence the new volume $= 125 \times \frac{258}{298} = 108.2$ c.c.

In practice, when a sample of gas is measured, we read the existing temperature, and correct the volume to that which the sample specimen would occupy at 0° C. For example, the volume is 102 c.c. at 18°, what is it at 0°? The absolute temperatures are $18 + 273 = 291°$ Abs., and $0 + 273 = 273°$ Abs. The new volume will be smaller. Hence, new volume = $102 \times \frac{273}{291} = 95.7$ c.c. This correction enables us to compare all volumes of gases as if they had been measured at the same, standard temperature, namely at 0°.

53. Corrections for Pressure and Temperature Combined. Since the volume-changes, due to alterations in pressure and in temperature, are independent of one another, the corrections may be made either separately, or together. The latter

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In solids and liquids these molecules are closely packed together. In gases, however, they are widely scattered, with much vacant space between them. A gas is in fact a vacuum, with numerous relatively minute particles scattered through it. When a gas is compressed, only the spaces *between* the molecules are reduced. By assuming further that, in gases, the molecules are in rapid motion, and produce pressure by striking the walls of the vessel, and that this motion is increased by raising the temperature, all the laws of gases can be completely explained.

This hypothesis was first stated in rather complete form by Lomonossov (1744–50), and later, independently, by Waterston (1845) and by Clausius (1857).

56. Exercises.

1. Show that, if the levels of the water inside and outside the tube (Fig. 14, p. 32) are alike, the pressure of the gas inside must be equal to the atmospheric pressure.

2. Find the volume that 48 c.c. of gas at 732 mm. would occupy at 760 mm.

3. Reduce 48 c.c. of gas at 780 mm. to standard pressure (760 mm.).

4. Find the volume which 28 c.c. of gas at 775 mm. would occupy if the pressure changed to 730 mm.

5. Find the volume which 320 c.c. of gas at 20° would occupy at 0° (pressure unaltered).

6. Reduce 600 c.c. at 25° and 760 mm. to standard conditions (0° and 760 mm.).

7. What change in volume would occur if 1 liter of gas at 200° were cooled to 0°?

8. Reduce 260 c.c. of gas at 10° and 742 mm. to standard conditions.

9. Reduce 35 c.c. of gas standing over water at 21° and 732 mm. to dry gas under standard conditions.

10. Give the feature of the molecular hypothesis which corresponds to each of the following facts about gases:

(a) A specimen of gas can be compressed to 1/2000th of the volume it occupies at 760 mm.

(b) A gas, even if heavier than air, gradually leaves an open cylinder.

(c) A specimen of a gas exercises pressure equally in all directions.

(d) Crowding the specimen of gas into one-third of its original volume triples its pressure.

(e) When the temperature is raised, the pressure of a specimen of gas increases (if the volume remains unchanged).

11. When we drink lemonade through a straw, what causes the liquid to flow up into our mouths?

CHAPTER VI.

HYDROGEN.

57. After considering the atmosphere, and particularly its most active component, we naturally turn to water, which, like air, is so closely associated with our daily life. We find that water is a compound of oxygen with hydrogen, and the latter element, therefore, next claims our attention. Hydrogen is of interest upon its own account. It is often used for filling balloons. Illuminating gas, of the kind (water gas) used in most large cities, consists of hydrogen to the extent of about 40 per cent.

58. Preparation by the Action of Metals on Water. Hydrogen is not easily liberated from water, since this oxide of hydrogen, like many other oxides, is very stable. It is necessary to use some element with which oxygen will combine even more eagerly than with hydrogen, and to offer this element in exchange for the hydrogen.

If a piece of one of the very active metals, such as *potassium, sodium, or calcium* (now obtainable in commerce) is *thrown into water,* hydrogen is liberated and comes off in bubbles. The former two metals are lighter than water, and run about on the surface. The action with potassium is so violent that the hydrogen usually catches fire, and both with sodium and potassium much heat is produced. The action often ends with a slight explosion, so that a glass plate should be held up to protect the eyes. This experiment is too dangerous to be tried by a novice. With calcium the action is rapid, but not violent, and there is no danger. The metal sinks to the bottom of the vessel (Fig. 15), so that a test-tube or bottle filled with water can be inverted over the metal to catch the gas as it ascends.

The metals, of course, act upon a small part only of the whole vesselful of water. In each case the metal displaces one-half of the hydrogen from that part of the water upon which it acts:

Sodium (23)	+	Water (18)	→	Hydrogen (1)	+	Sodium hydroxide (40).
		Hydrogen				**Sodium**
		Hydrogen				**Hydrogen**
		Oxygen				**Oxygen**

The products are hydrogen, along with potassium hydroxide, sodium hydroxide, or calcium hydroxide. In each case the name of the hydroxide indicates the composition, as including the metal along with hydrogen and oxygen. The first two hydroxides are very soluble in water, but most of the calcium hydroxide is not dissolved, and may be seen suspended (p. 12) in the liquid.

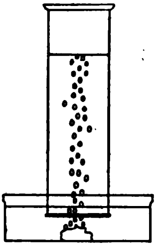

Fig. 15

Magnesium will liberate hydrogen from water, provided the latter is hot. If *steam* be passed through a heated tube containing *iron filings*, a mixture of hydrogen, with unused steam, issues at the other end. The magnetic *oxide* of iron (not hydroxide) remains in the tube:

Iron	+	Water	→	Hydrogen	+	Magnetic oxide of iron.
		Hydrogen				**Iron**
		Oxygen				**Oxygen**

This is a method much used in making hydrogen for commercial purposes.

Silver, gold, and platinum, which do not combine directly with pure oxygen, and even copper and mercury, which do, are all *unable* to form oxides and to liberate hydrogen when heated in steam.

59. Displacement. The foregoing actions, in which hydrogen is liberated, present us with a new — the third — variety of chemical change. Here **an element displaces one of the elements from a compound,** setting it free, and **unites with the rest of the constituents of the compound.** Thus, calcium displaces part of the hydrogen, and unites with the oxygen and the rest of the hydrogen.

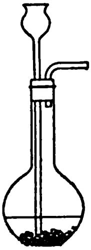

Fig. 16

60. Preparation by the Action of Metals upon Dilute Acids. All *the metals which displace hydrogen* from water or steam will also act upon *cold dilute acids* and *displace the hydrogen they contain.* This action is the one most commonly employed in the laboratory (Fig. 16). The gas, being much lighter than air, is collected by **downward displacement** of the latter (Fig. 17b). Heavy gases are collected by **upward displacement** of air (Fig. 17a).

Extremely pure zinc is almost inactive, but commercial zinc, on account of the contact action of the slight impurities it contains, gives a steady, not too violent, evolution of hydrogen. Sulphuric acid and hydrochloric acid, in each case diluted with water, are convenient acids. Iron shows about the same activity, but, on account of the impurities usually present in iron filings or wire, the hydrogen contains other gases which exhibit a distinct odor.

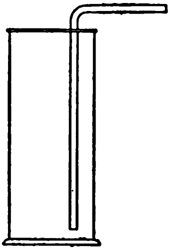

Fig. 17a

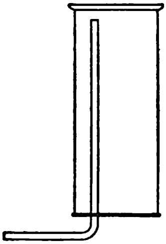

Fig. 17b

Zinc (65.4) + Sulphuric acid (98) → Hydrogen (2) + Zinc Sulphate (161.4).

$\textbf{Hydrogen}\left\{\begin{matrix}\textbf{Sulphur}\\ \textbf{Oxygen}\end{matrix}\right.$ $\qquad\qquad$ $\textbf{Zinc}\left\{\begin{matrix}\textbf{Sulphur}\\ \textbf{Oxygen}\end{matrix}\right.$

Iron (56) + Hydrochloric acid (72.9) → Hydrogen (2) + Ferrous chloride (126.9).

Hydrogen $\qquad\qquad$ **Iron**
Chlorine $\qquad\qquad$ **Chlorine**

It will be seen that the action is of the form we have called displacement (§59).

61. The Proportions by Weight. It may be well to remind ourselves that the weights of the various materials (given in brackets) are obtained by laboratory measurements. It is always found that the total weight of the product is exactly equal to that of the materials used (§ 35). Also, that a given weight of the metal, say zinc, will always displace and liberate the same weight of hydrogen. Also, that the proportions by weight of the constituent elements in the compound produced are always the same (§ 34). If we place a weighed piece of zinc in hydrochloric acid, and wait until the zinc has all disappeared, we can then boil away the water and unused acid, and weigh the white, solid zinc chloride. We find that 65.4 grams of zinc always leave 136.3 grams of zinc chloride. The difference, 70.9, is the chlorine, and whatever weights we take, the proportion of zinc to chlorine in the zinc chloride is always in the ratio 65.4 : 70.9.

Zinc (65.4) + Hydrochloric acid (72.9) → Hydrogen (2) + Zinc chloride (136.3).

Hydrogen 2 $\qquad\qquad$ **Zinc 65.4**
Chlorine 70.9 $\qquad\qquad$ **Chlorine 70.9**

62. Chemically Equivalent Quantities. It will be observed that 65.4 parts of zinc displace 2 parts of hydrogen, whether the acid used is sulphuric acid or hydrochloric acid. The proportion is, in fact, the same with every acid. Hence 65.4 parts of zinc and 2 parts of hydrogen are spoken of as **chemically equivalent** quantities. The quantities of the displacing and of the displaced element are in all cases referred to as chemically equivalent.

The term equivalents is applied also to the quantities *liberated by decomposition* of a compound, like the 100 parts of mercury and the 8 parts of oxygen (p. 24). It is likewise used of the proportions *combining* when chemical union takes place, as in the case of phosphorus 31 parts and oxygen 40 parts (p. 29). The proportions of the element in zinc chloride (p. 41) are also chemically equivalent.

Chemically equivalent quantities (or, simply, **equivalents**) of two substances are exact **quantities which enter into or result from a chemical reaction.**

63. The Order of Activity of the Metals. It will greatly aid us in remembering a number of the facts already given, as well as many others, if we compare carefully with those facts the order in which the metals stand in the adjoining list. The most active metals are at the top. All above hydrogen displace this element from dilute acids (and, with more difficulty, from water); those below it, do not.

ORDER OF ACTIVITY.
Metals.
Potassium
Sodium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Chromium
Iron
Nickel
Tin
Lead
Hydrogen
Copper
Bismuth
Antimony
Mercury
Silver
Platinum
Gold

The first displaces the hydrogen from water so violently that the gas catches fire, the second displaces it vigorously, the third less vigorously. Magnesium requires hot water and iron superheated steam. Copper and the metals following it do not liberate hydrogen from water.

Again, the upper metals act too violently on dilute acids, and zinc is used to prepare the gas. Copper and the metals following it do not displace hydrogen from dilute acids.

Still again, we recall the fact (p. 31) that, when we heat metals in pure oxygen, the last three do not become oxidized at all. Those preceding silver do combine with pure oxygen — mercury with difficulty, and the others more and more vigorously as we ascend the list. On the other hand, if we start with the oxides of all the metals, we find that those at the foot of the list, up to and including mercuric oxide, lose all their oxygen when heated, leaving the metal.

Other facts of a similar nature will be mentioned as we encounter them. Meantime, it may be noted that the metals found uncombined in nature are those following hydrogen. Again, the metals known to have been first used by the human race were gold and silver. In the "bronze age" means of liberating copper from its ores had been discovered. Lead, tin, and iron came later. The list, read from the bottom up, gives, therefore, roughly, the historical order in which the metals came into use.

64. Preparation by Electrolysis of a Dilute Acid. A convenient way of obtaining pure hydrogen is by *passing a current of electricity through a dilute acid* (Fig. 18). The gas is liberated at the negative wire (cathode) and collects in the tube (also filled with the dilute acid). The direct, 110-volt current, passing through a 16-c.-p. lamp placed in series with the electrolytic apparatus, may liberate 50 c.c. of hydrogen in 7-8 minutes. Every acid contains hydrogen, combined with other elements. The other elements are carried to the positive plate (anode), and therefore do not interfere with the collection of pure hydrogen. What may be liberated at the positive plate depends upon the acid used. With hydro-

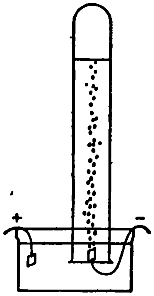

Fig. 18

chloric acid, it is chlorine; with sulphuric acid, oxygen comes off and sulphuric acid is regenerated.

Hydrochloric acid (in Aq. Soln.) → Hydrogen (neg. plate) + Chlorine (pos. plate).

The process is called **electrolysis,** from the Greek, meaning *decomposed by electricity.*

65. Physical Properties of Hydrogen. The gas is *colorless, odorless,* and *tasteless.* It is, bulk for bulk, the lightest known gas, the *density* of air being about 14.5 times as great. It can be *liquefied* by compression below −234° (its critical temperature). It *dissolves* in water to the extent of 1.8 volumes in 100 volumes of water at 15°.

The lightness of the gas may be shown by pouring it *upwards* from one jar to another (Fig. 19), or by balancing an inverted beaker with shot, and allowing hydrogen to flow in and displace the air (Fig. 20).

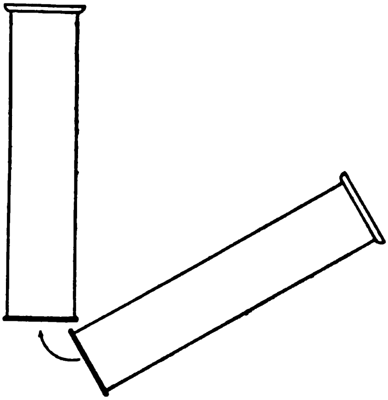

Fig. 19

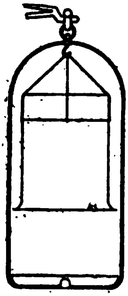

Fig. 20

Several metals can absorb ("occlude") hydrogen gas. Iron takes up about 19 times its own volume, platinum 50 volumes, and palladium from 500 to 800 volumes.

Liquid hydrogen, when allowed to evaporate rapidly, freezes to a colorless solid, which melts again at −260°.

66. Chemical Properties of Hydrogen. That hydrogen, when it *burns* in the air, forms water, was first shown by Cavendish (1781). A test-tube or beaker, filled with cold water and held over a flame of burning hydrogen, will condense the steam to droplets of water (Fig. 21).

Hydrogen + Oxygen → Water.

The union is very violent, so that when a mixture of hydrogen with pure oxygen is set on fire (they do not unite when cold) much heat is liberated in the explosion. The gases can be made to burn quietly, but with an exceedingly hot flame, by the use of an oxy-hydrogen burner (Fig. 22), which is constructed like a blast lamp. Iron melts and burns in the flame. A piece of quicklime, held in the flame, glows with a brilliant white light — the **calcium light** (Drummond light or lime-light). For such uses the gases are obtained in compressed form in iron cylinders (Fig. 23).

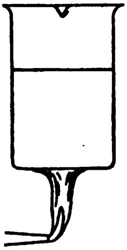

Fig. 21

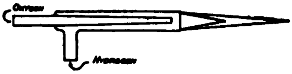

Fig. 22

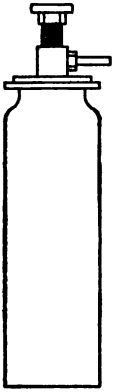

Fig. 23

Hydrogen combines vigorously with *chlorine*, giving hydrogen chloride, a gas of which hydrochloric acid is a solution. It unites with the three most active *metals* in the list (p. 42). Calcium hydride is sold under the name of **hydrolyte**, and is used, on account of its action on water, as a source of hydrogen.

Hydrogen *acts upon* many *compounds containing oxygen*, removing the latter to form water. Thus when the oxide of iron or of copper is heated in a tube in a stream of hydrogen, water is produced and the metal remains:

$$\text{Magnetic }\underset{\substack{\text{Iron}\\ \text{Oxygen}}}{\text{oxide}}\text{ of iron} + \text{Hydrogen} \rightarrow \text{Iron} + \underset{\substack{\text{Hydrogen}\\ \text{Oxygen}}}{\text{Water.}}$$

Oxides of metals above iron in the "order of activity" (p. 42), however, are very stable. Hydrogen is unable to remove the oxygen from such oxides and leave the metal.

67. Reduction. The removal of oxygen from a compound by its union with some other substance is called **reduction,** and the substance (in the foregoing instance, hydrogen) is called **a reducing agent.** Carbon, in the form of coal or coke, is the agent of this kind most commonly used in chemical industries. The term reduction is applied to some other chemical actions, in which oxygen is not concerned. In all cases, however, reduction is the opposite of oxidation (p. 29).

68. Exercises.

1. Name three varieties of chemical change (pp. 10, 20, 40) and explain the difference between them.

2. What do you infer as to the composition of a substance when it is named: (a) an oxide, (b) an hydroxide (p. 39)?

3. What are the equivalent quantities of: (a) carbon and oxygen (p. 29), (b) zinc and sulphur?

4. What law shows that the ratio of the chemically equivalent quantities of any two substances must be constant?

5. Name the metals which: (a) do not liberate hydrogen from water or dilute acids, (b) are found free in nature.

6. Why does hydrogen gas, when poured out, flow upwards? Why is it an excellent gas for filling balloons?

CHAPTER VII.

WATER.

69. If oxygen is necessary to the life of plants and animals, so also is water. The human body is saturated with it, and water to make up for evaporation, as well as to aid in digestion, is a most necessary part of our food. The ocean covers about three-fourths of the surface of the earth, and the "dry" land would be uninhabitable if it were really dry. The air always contains more or less water vapor.

70. Measurement of the Composition by Weight. An arrangement by which the proportion by weight of hydrogen and oxygen in water can be determined is shown in Fig. 24. The bulb *A* contains cupric oxide, which is heated. Hydro-

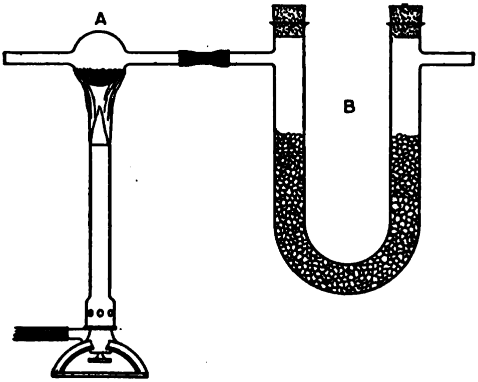

Fig. 24

gen from a generator or cylinder enters on the left and reduces the oxide, forming copper and water:

Hydrogen + Cupric oxide → Water + Copper.

The water is carried as vapor by the excess of hydrogen and passes into the U-tube *B*. This tube contains calcium chloride, a substance which absorbs water greedily and is used therefore for drying gases. Here the water is all caught, while the hydrogen passes on. The tubes *A* and *B* with their contents are weighed just before, and again just after, the experiment. The loss of weight in *A* is the weight of the oxygen. The gain in weight in *B* is the water. The difference between these numbers is the hydrogen. It is found that the weights of hydrogen and oxygen thus ascertained always stand in a ratio close to 1 (Hyd.) : 7.94 (Ox.) or 1.008 : 8, the proportion accurately determined by Morley.

Fig. 25

71. Measurement of the Composition by Volume. The proportions by volume in which hydrogen and oxygen combine may be shown by introducing the two gases into a tube, filled with mercury and inverted in a cylinder of mercury (Fig. 25). The volumes, at atmospheric pressure, are read by lowering the tube, after the introduction of each gas, until the levels of the mercury inside and outside are alike. A spark from an induction coil, passed between the platinum wires inserted at the top of the tube, causes the union of the gases. The water condenses to a slight dew and the volume of the single gas which remains is measured. Thus, if 19.5 c.c. of oxygen and 20 c.c. of hydrogen are taken, the volume of gas remaining is 9.5 c.c., and this gas is afterwards found to be oxygen (test, p. 29). The volumes consumed were therefore 19.5 − 9.5 = 10 c.c. of oxygen and 20 c.c. of hydrogen. The ratio by volume is therefore 1 Ox. : 2 Hyd. If these exact proportions are used, the mercury fills the tube after the explosion, but is apt to break it by striking the top violently.

By taking the gases in the exact ratio 1 : 2, and surrounding the tube by a wider one through which steam passes, the condensation of the resulting steam is prevented. It is found that, when all the gases are measured at the same temperature (here about 100°), a shrinkage of one-third occurs. That is to say:

$$1 \text{ vol. Ox.} + 2 \text{ vols. Hyd.} \rightarrow 2 \text{ vols. Steam.}$$

72. Gay-Lussac's Law of Volumes. When other chemical actions between gases are studied in the same way, it is found that, in every case, **the volumes of the gases used and produced in a chemical change can always be represented by the ratio of small whole numbers.** This fact is exceedingly interesting. It was first discovered by **Gay-Lussac** in 1808. There is no such simple relation amongst the proportions by *weight*, which usually can be expressed only by large numbers (see pp. 11, 29, 41) or by irregular fractions, so that this evidence of the existence of a simple rule in regard to combining proportions is the first we have encountered and is very welcome. The use made of it by the chemist will be developed in the next chapter.

73. Physical Properties. Water is without *odor* or *taste.* It is very pale blue in *color*, as is shown when we look through a considerable depth of water.

Melting ice and freezing water have the same temperature. The point at which the mercury column of a thermometer stands, when the instrument is immersed in such a mixture of ice and water, is marked 0° on the centigrade scale. This is the *freezing-point* of water. The *density* of ice is little over nine-tenths that of water.

When water is heated, it gives off vapor more and more freely until finally it boils. This point is recognized by the fact that bubbles of vapor form within the liquid, rise through it, and burst on the surface. The temperature of the water (if it is pure), and of the steam, are now found to be identical, and this thermometer reading is marked 100° C. — the *boiling-point.* Water is thus the standard substance used in the graduating of thermometers. When so used for fixing the temperature of 100°, the atmospheric pressure must be normal, that is 760 mm., for the temperature of boiling is lower when the pressure is lower.

When water has reached the boiling-point, the temperature ceases to rise, and the heat supplied is used in changing the water into steam. The evaporation of 1 gram of water consumes 540 heat units or calories (**heat of vaporization**). The melting of 1 gram of ice consumes 79 calories (**heat of fusion**). The **calorie** is the average amount of heat required to raise 1 gram of water one degree in temperature between 1° and 100°.

The amount of heat required to raise the temperature of a given mass of water one degree is greater than that required for an equal mass of any other common material. Hence, the temperature of the sea changes more slowly, and within a smaller range, than that of the rocks which compose the land. For this reason the climate of islands surrounded by much water is less variable from season to season within the year than is that of the continents.

74. Steam. The quantity of vapor given off by water at various temperatures is best measured by the gaseous pressure it exercises. A little water introduced into a barometric vacuum (*B*, Fig. 26) will depress the mercury, and the difference in height is a measure of the vapor pressure of the water. The temperature may be changed by putting hot water into the tube surrounding the barometer, and thus the increase in vapor pressure with rising temperature may be shown. At 0° the column of mercury is depressed 4.6 mm., at 10° the vapor pressure becomes 9.2 mm., at 20° 17.4 mm. (see Appendix IV). At 100° the level of the mercury in the tube would be depressed 760 mm., and would sink to the level of that in the trough. If a little air is first placed above dry mercury, causing it to fall, the *additional* depression produced by adding water is the same as if the air had been absent (p. 35).

Steam at 100°, subjected to a pressure over one atmosphere, is condensed to water. Steam cannot be condensed by pressure, however, if the temperature is over 358°, its critical temperature. At 100° the steam occupies more than 1700 times the volume of an equal weight of water.

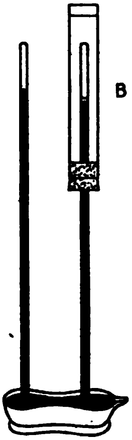

Fig. 26

Steam is a perfectly invisible gas. The visible cloud of fog, issuing from a valve when steam escapes, is composed of minute drops of water, formed by condensation.

75. The States of Matter. Most substances are known in at least three different states, namely, a solid, a liquid, and a gaseous form. There is no magic about the number three, however. Very many substances are known in more states than three. Thus sulphur has a vapor state, two liquid states, and several different solid forms. There are even five different forms of ice, and it seems probable that all solids can exist in several different solid states.

With all substances the changes from a solid to a liquid, and from a liquid to a gaseous state, always take place at some definite temperature, similar to the melting-point of ice and the boiling-point of water.

76. Water as a Solvent. Water has a remarkable power of *dissolving* many other substances, and is said, therefore, to have great power as a *solvent.* In the simplest cases, at least, the operation appears to be purely mechanical and this is classed therefore as a physical property.

77. Natural Waters. Rain is the *purest* natural water. As it is formed by condensation of water vapor, and has been in contact with the atmosphere only, it contains only oxygen and other gases dissolved from the air, together with a little dust. Sea water contains the *greatest amount of dissolved material,* namely about 3.5 per cent. River and, especially, well waters contain materials in solution which have been dissolved from the soil and the rocks. These materials act chemically upon soap so that well waters are more or less hard, while rain water is soft. We have already learned (p. 30) that natural waters may also contain bacteria, which give rise to putrefaction and disease. Many river waters contain large amounts of clay and other insoluble substances suspended in them. The suspended matter can be seen, as it renders the water turbid, but the bacteria are invisible, and organic matter and bacteria may be present in waters which look perfectly clear.

78. Purification of Water. The *suspended impurities,* including the bacteria, may be removed by **filtration.** City waters are often filtered through extensive beds of gravel, but this treatment will not remove all bacteria. In many cases, small amounts of alum, or alum and lime, are added to the water, and the suspended matter is then allowed to settle, which it does very quickly, in large basins or reservoirs. By this **coagulation method** (§ 562), all but a few of the bacteria are removed. Sometimes the remaining organisms are destroyed by adding a little bleaching powder before the water is distributed (§ 377).

In the household, the simplest appliance is the **Pasteur filter.** It consists of a tube of unglazed porcelain, closed at one end (Fig. 27), through the pores of which the water is forced inwards by its own pressure. The cylinder ("bougie") should be cleaned daily with a brush to remove the mud and the organisms which collect in its outer surface.

All forms of filters must be *cleaned* at short intervals. If this is not done, the organisms multiply and soon the filter pollutes the water instead of purifying it.

Filtration does not remove *dissolved matter,* and therefore does not soften hard water (§ 531). For this latter purpose washing powders are used in the laundry (see § 534).

All *organisms* can be killed by boiling unfiltered water, but the boiling should continue for at least 10 to 15 minutes to be effective, and a later, second boiling is needed in some cases.

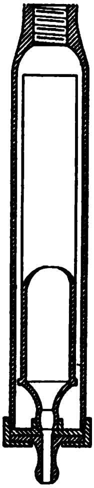
Fig. 27

Pure water for chemical purposes is prepared by **distillation** (Fig. 28). Dissolved solids remain in the flask. The steam is condensed by cold water circulating in the jacket of the condenser. Freshly distilled water contains only gases dissolved from the air. If kept in a vessel, however, such water quickly dissolves traces of glass or porcelain. The purest water is made by using a platinum tube in the condenser and a platinum bottle as the receiver.

79. Chemical Properties: Stability. As we should infer from the vigor with which its constituents combine, water is a very *stable* substance. When steam is superheated, hardly a trace of decomposition occurs. Even when the temperature reaches 2500° (far above a white heat), only 1.8 per cent of the vapor is broken up into oxygen and hydrogen. When the steam cools, these elements recombine:

$$\text{Water} \rightleftarrows \text{Hydrogen} + \text{Oxygen}.$$

Water is so frequently used simply to dissolve chemical substances that we should note carefully the cases (see §§ 80 and 82, following), which are relatively few, in which it enters into chemical action.

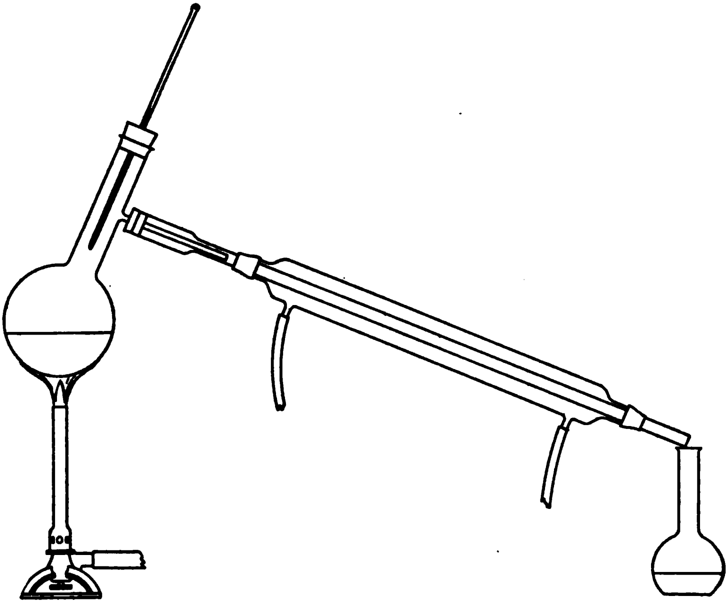

Fig. 28

80. Hydrates.

80. Hydrates. Many substances unite with water to give compounds called **hydrates**. Thus if we take zinc sulphate (p. 41) and dissolve it in water, and allow the excess of the latter to evaporate, the solid appears in long transparent crystals. When these are dried with blotting paper and heated in a test-tube, they give off a large amount of steam. The hydrate of zinc sulphate decomposes and leaves *anhydrous* (Greek, *deprived of water*) zinc sulphate. The latter, when once more moistened, changes back into the hydrate.

Zinc sulphate + Water ⇄ Hydrate of Zinc sulphate.

Many common chemicals are in fact such hydrates. Thus common blue-stone, used in gravity batteries, is a hydrate of cupric sulphate. When heated, it loses water and leaves the colorless, anhydrous cupric sulphate. These are cases of simple combination and decomposition.

81. Efflorescence. Some hydrates are so unstable that the water passes off, even at room temperature, when the hydrate is left in an open vessel. Thus crystals of washing soda (hydrate of sodium carbonate) crumble to powder (**effloresce**) *when not kept in a closed vessel.*

Sodium carbonate + Water ⇄ Hydrate of Sodium carbonate.

If a crystal of a hydrate like this is placed in the barometric vacuum (Fig. 26, p. 51) it is found to give a considerable vapor pressure of water, so that its tendency to decompose, when the vapor is allowed to escape, is easily understood. The measured pressure of water vapor coming from such hydrates at ordinary temperatures is found to be greater than the average pressure of water vapor in the atmosphere.

On the other hand, when anhydrous cupric sulphate and zinc sulphate, obtainable from the hydrates by heating only, are spread out in the air, they return slowly to the hydrated condition. They combine with the moisture in the air. The vapor pressure of water in the air is greater than the vapor pressure of water which these hydrates give off at ordinary temperatures. Calcium chloride absorbs water vapor (p. 48) because of its tendency to form a hydrate.

82. Other Chemical Properties. The cases where water combines directly with oxides (§§ 252, 348–9, 524, 527), and where it acts chemically upon substances dissolved in it (§ 466) will be noted later.

83. Reversible Chemical Actions. The contrary effects upon an unstable hydrate of leaving the bottle open or closed, referred to in § 81, deserves a moment's notice. When understood, it explains many things in chemistry. The hydration and dehydration are opposite directions of the same chemical change, and the condensed statements of the actions were written with the **double arrow** to indicate this (§ 81). When the bottle is closed, the water vapor is unable to escape and recombines with the anhydrous particles as fast as other particles of the hydrate decompose. **A reversible action** therefore **can not complete itself, if the products of the action are kept together and not allowed to separate.** On the other hand, **a reversible action will go to completion, if one of the products escapes,** as the water vapor does when the bottle is left open. This idea enables us to answer several interesting questions.

For example, why does steam decompose to the extent of 1.8 per cent at 2500 degrees, but not any further? All its parts are alike and are therefore equally *capable* of decomposing. The answer is, because neither the oxygen nor the hydrogen is removed, or can easily be removed, from the steam, and so the completion of the decomposition is prevented by continual *recombination of these gases.*

When a reversible action has come to a standstill, we say that **equilibrium** has been reached. This means that two opposing tendencies are neutralizing each other's effects.

When will reversible actions go to completion? The products must be of such a nature that they *separate easily*. In practice, this happens when *one is a gas or vapor*, like the water vapor coming from a hydrate, while the other is not. The *settling of one product as a precipitate*, while the other stays in solution, is, as we shall see (§ 144, 145), another common way in which the separation occurs.

When iron and water are heated in a *closed* vessel (p. 39), the hydrogen and oxide of iron which are produced react with one another (p. 46) to give back water and iron:

$$\text{Iron} + \underset{\substack{\text{Hydrogen} \\ \text{Oxygen}}}{\text{Steam}} \rightleftarrows \text{Hydrogen} + \underset{\substack{\text{Iron} \\ \text{Oxygen}}}{\text{Magnetic oxide of iron.}}$$

In a closed vessel we could never use this method for preparing any quantity of hydrogen. To prepare hydrogen (p. 39) by this action we leave the tube open, and let the steam *sweep the hydrogen out*. This separates it effectually from the oxide of iron, and prevents the reversal of the action.

Devices depending on mechanical principles like this are continually used in chemistry for securing easy methods of preparing substances.

The reader can now answer for himself the question why we are able to prepare oxygen by heating mercuric oxide (p. 24), in spite of the fact that the action is reversible (p. 20).

84. Exercises.

1. If 50 c.c. of hydrogen and 37 c.c. of oxygen are exploded in a closed tube, which gas remains and what volume of it is left?

2. Why do not bubbles of steam ordinarily form in water and rise through it at temperatures below 100°?

3. How many calories of heat would be required to change 5 grams of ice at 0° into steam at 100°.

4. How could one find out how much solid matter was dissolved in a sample of water?

5. Define: filtration, distillation, efflorescence, chemical equilibrium.

6. Explain how water, even at room temperature, gradually dries up (p. 51).

7. Why does a strong wind hasten the evaporation of water?

8. Why does the lower surface of a sheet of ice on the pavement melt in the sun before the upper one?

CHAPTER VIII.

CHEMICAL UNITS OF WEIGHT. FORMULÆ.*

85. As we have seen (p. 49), when the *volumes* occupied by substances in the gaseous condition, rather than the weights, are taken as the basis of measurement, the combining proportions are *simple* and are expressible by *small whole numbers* (Gay-Lussac's law). This shows that there must be some relationship, *connected with chemical combination*, between the amounts of *different* substances contained as gases in equal volumes. It suggests that we might do well to take such amounts (weights of equal volumes) as the standard or unit quantities for chemical purposes. Now this is precisely what the chemist has found it in practice most convenient to do, and the present chapter deals with the units of material based upon comparing equal volumes.

86. Illustrations of Gay-Lussac's Law. Let us first familiarize ourselves with the volume-measuring point of view in chemical actions. The following are a few observed facts, beginning with the union of hydrogen and oxygen already discussed (pp. 48–9):

(1) Hydrogen (2 vols.) + Oxygen (1 vol.) → Steam (2 vols.).
(2) Hydrogen (1 vol.) + Chlorine (1 vol.) → Hydrogen chloride (2 vols.).
(3) Chlorine monoxide (2 vols.) → Chlorine (2 vols.) + Oxygen (1 vol.).
(4) Mercuric oxide (not volatile) → Mercury (2 vols.) + Oxygen (1 vol.).

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* If deemed desirable, the systematic study of this chapter may be omitted. The various conclusions reached in it may be briefly explained as each comes into use in later chapters.

(5) Phosphorus (1 vol.) + Oxygen (5 vols.) → Phosphorus pentoxide (1 vol.) (see § 119).

(6) Zinc (at 1000°, 2 vols.) + Sulphur (at 1000°, 1 vol.) → Zinc sulphide (at 1000°, not volatile) (see § 118).

It will be noted that in some cases, like (2), there is no change in the total volume. In others there is a shrinkage, as in (1) and (5). In still others, like (3), where chlorine monoxide decomposes, there is an increase in volume. In (5), in order that all the materials may be gaseous, the whole experiment must be done at a very high temperature (and at some suitable pressure). In (4) the mercuric oxide itself does not become gaseous, but decomposes, so that its own relative volume cannot be given. In (6) the zinc and sulphur can be combined as vapors at 1000°. The product (zinc sulphide) will not remain gaseous at any temperature at which its volume can be measured, however, and so its volume is not recorded.

It must be kept constantly in mind that the law *applies to volumes in the state of gas or vapor only*. There is no rule about the proportions by volume required for the chemical combination of liquids and solids.

One can read these illustrations in different ways. For example: (1) a given volume of steam is formed by union of the same volume of hydrogen with half as great a volume of oxygen. (4) Mercuric oxide, when decomposed by heating, gives two volumes of mercury vapor and one volume of oxygen in every three volumes of the escaping gases. (5) One volume of phosphorus vapor, together with an equivalent quantity of oxygen, will give one volume of the vapor of phosphorus pentoxide, all being measured at the same temperature. In fact, whenever two vaporizable substances are amongst the factors and products of a chemical change, their volumes thus are either equal, or are to one another in the ratio of whole numbers.

87. The Standard or Unit Volume. The volumes in the foregoing paragraph are simply relative, and the statements are true of gaseous volumes of any actual dimensions (large or small), provided only they bear the proper *relationship*, such as 2 : 1, 1 : 1, or 1 : 5, in each case. An actual value has been chosen, however, for the volume which is the standard or unit in chemistry. This is **22.4 liters** at 0° and 760 mm. This volume is equal to that of a cube about 11 inches in height (Fig. 29). At other temperatures and pressures this volume, in order to contain the same amount of material, alters its value, in accordance with the laws of Boyle and Charles (p. 33). The reason for selecting this particular volume (see § 98) will be readily seen, so soon as we shall have presented the actual weights of various materials which fill it.

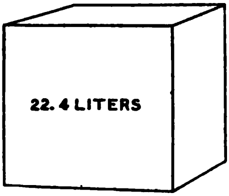

Fig. 29

88. The Weights Filling the Unit Volume, 22.4 Liters. The following table contains a few sample substances, and gives the weight (in grams) of each which, in the gaseous condition, at 0° and 760 mm., occupies the cube — 22.4 liters. In the cases of compound substances, like water, we have given also the weights of the constituent elements which together make up the total weight of the compound filling the unit volume:

Weights of Gases in 22.4 Liters (at 0° and 760 mm.).

Substance.	Total wt.	Wt. ox.	Wt. hyd.	Wt. chlor.
Oxygen	32	32	....	....
Water	18.016	16	2.016	....
Hydrogen	2.016	....	2.016	....
Hydrogen chloride	36.468	....	1.008	35.46
Chlorine	70.92	....	....	70.92
Chlorine monoxide	86.92	16	....	70.92

The first column ("Total wt.") gives the number of grams of each substance occupying, as a gas, 22.4 liters at 0° and 760 mm. This is the **standard** or **unit weight of that substance.** In the case of water, which is a liquid at room temperatures and pressures, a known volume of *steam* is weighed. The volume is reduced by rule to 0° and 760 mm., and the weight of 22.4 liters is calculated from the reduced volume and the measured weight.

The standard or unit weight (one cubeful) of a substance is commonly called its **molecular weight** (see § 100).

89. Unit or Standard Weights of the Elements. Let us now examine the weights of the constituent elements making up a cubeful of each substance, as shown in the last three columns of the above table. We must first be sure we understand what these numbers are. They are combining proportions, such as we have given on previous occasions (*e.g.* pp. 11, 14, 21). They are equivalents (p. 41). We can use them in our condensed form for representing chemical changes:

Oxygen (16) + Hydrogen (2.016) → Water (18.016).
Hydrogen (1.008) + Chlorine (35.46) → Hydrogen chloride (36.468).

We observe at once that the weights in the oxygen column, or the chlorine column, for example, are not identical. There was no reason to expect that they would be alike, since different substances differ in composition. But we do observe that *the weights of any one element are all multiples of one of the numbers, either by unity or some other whole number.* Thus, for hydrogen, the weights are: 1.008, 2.016 and 2.016. The unit weight of hydrogen chloride contains one unit of hydrogen, those of water and of hydrogen itself two units each. This is a very surprising, natural fact, and, better still, one for which we instantly perceive a use. This fact greatly simplifies our task of finding some way of expressing the compositions of substances in a simple manner. The fact does not apply to a few compounds, only. If our table had included all the hundreds of compounds of chlorine (for example) which are capable of being converted into vapor, we should have found, indeed, many multiples of 35.46 larger than the two units (70.92) in chlorine monoxide, but no number smaller than 35.46 and none which was not a multiple of 35.46 by a whole number. Clearly we shall find it convenient to accept 35.46 as the unit or standard weight of chlorine for expressing the compositions of its chemical compounds. Its use will enable us to state the exact composition of any given compound by simply *giving the whole number* (1, 2, 3, etc.) by which the *basal weight* 35.46 *is to be multiplied* in the given case.

Similarly, we take 1.008 as the unit weight of hydrogen and 16 as the unit weight of oxygen. By including volatile compounds of other elements in our investigation, we can similarly pick out the most convenient unit for each element. Those unit weights for elements are often called also **combining** or **reacting weights,** and still more frequently **atomic weights** (see § 103). A complete list of their values for all the known elements is given in a table inside the rear cover of this book. These numbers will hereafter be in constant use.

90. The Case of Non-volatile Compounds. The same elements enter also into many compounds which are not volatile. But the unit weights of such elements, determined by the use of volatile compounds, are found (by using multiples, when necessary) to express the composition of the involatile compounds also.

For example, the unit weight for oxygen (16) and that for tin (119), both learned by studying volatile compounds, are found correctly to express the composition of oxide of tin (§18), which is not volatile. The proportion of tin to oxygen already given, 100 to 26.89 (§ 19), can also be expressed exactly in terms of the units as 119 to 2 × 16.

In the cases of some elements no easily vaporizable compound is known, and the unit weight cannot be determined by the present method. In such instances, an entirely different way of obtaining the value of the unit weight is employed (see § 105).

91. The Law of Combining Weights. The general fact which we have developed in this and the preceding sections is known as the law of combining weights: **All the proportions in which the elements combine with one another may be represented by a set of numbers** (one for each element) **or by multiples of these numbers by whole numbers.**

92. Definition of Reacting or Atomic Weight. *Many different* values for each element would satisfy the law of combining weights. The particular values chosen as units fulfil an *additional condition* which fixes the value in each case, absolutely. The chosen **reacting** or **atomic weight** of an element is **the smallest weight of the element found in 22.4 liters** (at 0° and 760 mm.) **of the vapor of any volatile compound of that element.** The amounts of the element in 22.4 liters of other compounds are all either the same amount or multiples thereof by a whole number.

That the law of combining weights (§ 91) applies to these reacting weights, is very satisfying. This fact gives us reasonable assurance that, when a new compound is discovered, its composition will be capable of being expressed in a simple form, by using a suitable multiple of the reacting weight of each constituent element. The reacting weights of the different elements are all different (see table), but the unit for a given element has the same value in all compounds of that element.

93. Simplification of Condensed Expressions for Chemical Actions — Symbols. Our condensed expressions for chemical changes showed the name of each substance and also weights to indicate the combining proportions. Having now found a unit weight for each element, we can condense the statement still further, *by using a letter or pair of letters*, called a **symbol,** *to stand for one chemical unit weight of each element.* Thus O stands for one unit or 16 parts of oxygen, H for one unit or 1.008 parts of hydrogen, Cl for one unit or 35.46 parts of chlorine. A pair of letters is required when the names of several elements begin with the same letter. Thus, C stands for 12 parts of carbon, Ca for 40 parts of calcium, Cr for 52 parts of chromium, each of these amounts being one chemical unit of the element. These symbols are international, and are alike in all languages. In some instances they are based upon the Latin name for the element. Thus, Fe stands for 55.84 parts of iron (*ferrum*), Sn for 119 parts of tin (*stannum*), Ag for 107.88 parts of silver (*argentum*) and Hg for 200.6 parts of mercury (*hydrargyrum*). Again K stands for 39.1 parts of potassium (Ger. *kalium*) and Na for 23 parts of sodium (Ger. *natrium*).

94. Formulæ. The *composition* of a substance* can be shown briefly by putting together the symbols of the constituent elements, and using numbers for the multiples of the unit weights, where such are required. The resulting expression is called a **formula.** Thus water (table, p. 61) contains oxygen 16 parts (O) and hydrogen 2.016 parts ($= 2 \times 1.008 = H_2$), and receives the formula H_2O. Hydrogen chloride (p. 61) contains hydrogen 1.008 parts (H) and chlorine 35.46 parts (Cl), and its formula is HCl.

It must be noted particularly, that the *formula*, to be con-

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* The **composition** means the names of the elements contained in the substance, and *also* the proportion by weight of each element.

sistent, *must represent also the total weight of the unit quantity of the substance* (wt. of 22.4 l.). Thus, HCl (1.008 + 35.46 = 36.468) is correct, since 36.468 g. is the amount filling the cube. Again, the formula for oxygen gas itself must represent 32 g. (= 2 × 16), the weight of 22.4 l., and is therefore O_2. Half as much as this may enter into a compound, H_2O, ZnO, etc., but, logically, the formula for free oxygen must record the double weight required to fill the cube when the gas is present alone, in the free condition. Similarly, the formula for hydrogen gas is H_2 ($2 \times 1.008 = 2.016$, the weight of 22.4 l.). *The formula of every volatile substance must thus be written so as to show the weight of the chemical unit quantity* (the molecular weight, § 88). When the substance is not easily volatilized, this unit cannot be measured, and the simplest formula is employed.

95. Information Contained in Each Formula. A formula thus contains, in condensed form, several items of information. It shows:

1. The elements making up the substance,
2. The proportion by weight of those elements,
3. The total unit weight (molecular weight) of the substance. Given the formula, we can read these facts in it.

Thus, if we are given the formula of carbon dioxide, CO_2, we consult the table of reacting or atomic weights (inside rear cover), and learn that C = 12 *parts* by weight of *carbon* and $O_2 = 2 \times 16$ *parts* by weight of *oxygen*. The proportion by weight of the elements in this compound is, therefore, 12 of carbon to 32 of oxygen. The total weight (molecular weight) is $12 + 32 = 44$, and this must be the weight filling 22.4 l. (at 0° and 760 mm.).

96. Equations. Finally, a revised form of the condensed statement for a chemical reaction is prepared. Thus, for the union of hydrogen and oxygen, we write, first, the formulæ of the substances:

Skeleton equation: $H_2 + O_2 \rightarrow H_2O$.

This shows the unit quantities of each individual substance, but not necessarily the correct proportions in the particular action in question. Thus, $H_2 : O_2$ is equivalent to 2.016 : 32, whereas the correct proportion (p. 61) in this action is 2.016 : 16, or 2 × 2.016 : 32. Also, O_2 contains enough oxygen for $2H_2O$. The statement must therefore be adjusted ("balanced") to take account of these two facts. The correct equation for the action is therefore:

Balanced Equation: $2H_2 + O_2 \rightarrow 2H_2O$.

The final statement is called an equation because the weights of *each element* on the two sides are *equal*, and the *total weight* on each side is the same. This is in accordance with the law of conservation of mass (p. 21), which holds for all chemical changes.

97. Further Discussion of the Same Subject. At this point we have completed the explanation of the derivation of the units of weight, and of the symbols and formulæ used in chemistry. We are now in a position to proceed with the application of these conceptions, as they are developed in the next chapter. This would be possible, at least so far as strict logic is concerned. But, in shaping our course so as to reach the results by the shortest route, we have omitted a number of interesting and useful ideas. These were not indispensable links in our reasoning, but, now that we have covered the essential steps, a consideration of these ideas will be of great value as a review of the subject and a means of mastering it thoroughly. Formulæ and their uses come up so constantly in every part of the science that we must not omit any means of securing a perfect understanding of them. The following sections are therefore devoted to restating in other ways certain parts of the same subject.

98. Why was 22.4 Liters Chosen as the Unit Volume? It was chosen of such dimensions that no element should receive a unit weight smaller than unity. Hydrogen is the element which enters in the smallest proportions into chemical combination. In 22.4 l. of some compounds there is as little as 1.008 g. of this element (see table, p. 61). Any size would have served the purpose equally well — theoretically. But one much smaller than 22.4 l. would have held a weight of hydrogen chloride (*e.g.*) containing less than one gram of hydrogen.

If 22.2 l. had been chosen, this would have contained exactly 1 g. of hydrogen (in combination with 35.2 g. of chlorine). This volume was, in fact, at one time, the standard. But its use reduces all the numbers in the same proportion, and the unit weight of oxygen (in water, for example), then becomes about 15.9. The chief advantage of the scale O = 16 is that, on this scale, very many of the atomic weights happen to lie so close to whole numbers (see table) that the nearest whole number can almost always be used. This simplifies our calculations.

The accepted scale is, therefore, that of 32 for the unit weight of oxygen gas; 22.4 l. (the volume of 32 g. of free oxygen) for the chemical unit of volume; and 16 for the unit weight of oxygen in compounds containing that element. The unit weights of all the other compounds and elements are based upon this scale.

99. Application of the Molecular Hypothesis in Chemistry — Avogadro's Hypothesis. We have seen (§ 55) that the physical behavior of matter, and particularly of gases, is explained by the conception that matter is composed of molecules. The easy *compressibility* of gases is explained by the smallness of the molecules and relative vastness of the empty space between them. *Diffusion* is explained by the continual motion of the molecules, and *pressure* by the innumerable blows which the molecules deliver when they strike the boundary walls of the space in which the gas is confined. Now, when gases interact chemically, the volumes required for complete interaction are either equal or stand in the ratio of small whole numbers. This law (Gay-Lussac's) we illustrated in detail in the beginning of this chapter (§ 86). Although that is a chemical, and not a merely physical fact, the molecular hypothesis can explain it also.

Since matter is composed of molecules, a chemical action between two kinds of matter must consist really in an interaction of the molecules of each kind. Molecules of the two kinds must meet and they may then either *combine* to form a compound molecule, or they may *exchange* material in some fashion. Since equal volumes are often the exact quantities required for the action, it appears most likely that **in equal volumes of different gases** (at the same temperature and pressure) **the numbers of molecules present are equal.** This addition to the molecular hypothesis was first suggested by an Italian physicist, Avogadro (1811). When two gases interact in equal volumes (like hydrogen and chlorine, p. 59), one molecule of each is all that is required for a small sample of the change in question. Since two volumes of hydrogen are required to unite with one volume of oxygen (p. 49), clearly the interaction involves two molecules of hydrogen for every one of oxygen. Since two volumes of steam are produced, evidently the two molecules of hydrogen and one of oxygen yield two molecules of water.

This hypothesis of Avogadro helps us to a clearer notion of how these chemical changes take place. The idea that all gases contain equal numbers of molecules in equal volumes also explains why *all* gases behave alike when subjected to equal pressures, or to equal changes in temperature (Boyle's and Charles' laws, p. 33). No facts which conflict with this hypothesis are known, and all the known facts confirm it. Hence, Avogadro's hypothesis has been accepted by chemists, and since 1858 has been the keystone of chemical theory.

100. Consequences of Avogadro's Hypothesis — Molecular Weights. Equal volumes of the *same* gas (at the same temperature and pressure) have equal weights. But equal volumes of *different* gases have different weights. The differences are often very great. Thus, bulk for bulk, oxygen is sixteen times as heavy as hydrogen, and hydrogen iodide sixty-four times as heavy. Now, if equal volumes of different gases contain equal numbers of molecules, these differences must be due to the differing weights of the several kinds of molecules. Thus, measuring the weights of equal volumes of different gases will give us the relative weights of their molecules. For example, since 22.4 l. of oxygen weigh 32 g. (p. 61), while the same volume of hydrogen weighs 2.016 g. and of hydrogen chloride 36.468 g., and these are the weights of equal numbers of molecules, the individual molecules must differ in weight in the ratio 32 : 2.016 : 36.468. These are the relative weights of the three kinds of molecules. In chemistry the weights of 22.4 l. (at 0° and 760 mm.) of various gases are called the **molecular weights** of those gases. The unit quantities of various substances (§ 88) are therefore spoken of, technically, as the molecular weights of those substances. The unit volume, 22.4 l., is called the **gram-molecular volume** (G.M.V.).

The number of molecules actually contained in the G.M.V. is approximately 6 followed by 23 zeros, which we may write

60_{23}. The gram-molecular weight of any gas is therefore the weight in grams of 60_{23} molecules of the gas.

101. Molecular Weight, Measurement of. The molecular weight is *measured* by weighing any convenient volume of the gas (say 200 c.c.), and calculating by proportion the weight of 22.4 l. If the gas or vapor was not measured at 0° and 760 mm., the measured volume must be reduced by rule to standard conditions before the weight of 22.4 l. is calculated.*

For example, 190 c.c. of a gas at 0° and 760 mm. weigh 1.23 g. If x be the weight of 22.4 liters (= 22,400 c.c.),

$$190 : 1.23 :: 22{,}400 : x\ (= 145\text{ g.}).$$

Again, 210 c.c. of a vapor at 100° and 743 mm. weigh 1.12 g. This volume at 0° and 760 mm. would become:

$$210 \times \frac{273}{373} \times \frac{743}{760} = 150.3\text{ c.c.}$$

and

$$150.3 : 1.12 :: 22{,}400 : x\ (= 167\text{ g.}).$$

102. Molecular Weight and Density. Density is the term used in physics for the weight of 1 cubic centimeter of a substance. Thus, the density of water at 4° C. is 1, because at 4° C., 1 c.c. of water weighs 1 g. The density of ammonia gas (wt. of 1 c.c. at 0° and 760 mm.) is 0.000759 g.

Since the molecular weight is the weight of 22.4 l., or 22,400 c.c., the molecular weight of a gas is obtained by multiplying the density (if known) by 22,400. Thus, the molecular weight of ammonia is $0.000759 \times 22{,}400 = 17.0$.

Densities are often given on the scale, density-of-air = 1. Now 22.4 liters of air weigh 28.95 g. If a gas has a density

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* In practice, owing to the fact that Boyle's and Charles' laws do not describe the behavior of any known gas *exactly* (they apply only to a "perfect" gas), certain additional, small corrections have to be applied when very precise values are required.

twice that of air, 22.4 liters of this gas would weigh 28.95 × 2 g. For example, the density of carbon dioxide (air = 1) is 1.52. The molecular weight is therefore 28.95 × 1.52, or 44.0.*

103. Atomic Weights. Since a compound substance can be formed by union of the elementary substances, and decomposed to give these substances, its molecule may be assumed to contain those constituent elements as *distinct parts* of the mass. Those elementary parts of a molecule are called **atoms.** When two elementary substances combine, the process involves the union of the two kinds of atoms to form compound molecules. Now, in the table (p. 61), we recorded the weights of the constituent elements which together made up the molecular weights of the compounds. Then, upon examining the weights of any one element contained in molecular weights of different compounds, we saw (§ 89) that one (the smallest) could be taken as the unit weight, of which the others were multiples by some whole number. Obviously then, if the molecular weights are the relative weights of different kinds of molecules, the unit weights of the elements (35.46 for chlorine, etc.) are the relative weights of the atoms of the different elements. The relative weights of the different kinds of atoms, such as 1.008 for hydrogen, 16 for oxygen, 35.46 for chlorine, are called the **atomic weights** of the respective elements. These weights, as we have seen (§ 98), are relative to the weight of the atom of oxygen, when the weight of the latter is taken as 16, and the weight of the molecule of oxygen is taken as 32.

A compound molecule may contain one, or more than one, atom of each of the elements forming the compound. In the molecular weights of compounds, weights of elements which

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* This weight of carbon dioxide contains 12 parts of carbon (one atomic weight) and 32 parts of oxygen (two atomic weights) — total 44.

are smaller than the atomic weight (p. 61), or are not multiples of the atomic weight by a whole number, are not found to occur (see *e.g.*, p. 72, footnote). This indicates that, in chemical change, fractions of atoms play no part. The name atom (Greek, *not cut*, or *not divided*) records this fact.

104. The Atomic Hypothesis and Definite Proportions. The idea of atoms furnishes at once an explanation of the law of definite proportions. Evidently, *every molecule of a given substance must always contain the same numbers and the same kinds of atoms*, so that the proportions by weight of the constituents of the compound as a whole *must* be alike in all samples.

105. Dulong and Petit's Law. When an element gives no volatile compounds, as is the case with calcium, we can still find the atomic weight. We first find for the element an equivalent weight (p. 41). Thus, the weight of calcium which combines with 35.46 parts of chlorine is 20 parts. This weight, or some multiple of it by a whole number, does in fact always correctly represent the amount of calcium combined with atomic weights of elements whose atomic weights are known. Hence 20, or some multiple of 20, is the required atomic weight. Dulong and Petit (1819) discovered a rule by which the correctness of such an atomic weight could be checked. **When the atomic weight of an element is multiplied by the specific heat of the element in the solid form, the product is roughly 6.4.** Thus, the known atomic weight of magnesium is 24.3, its specific heat 0.245, and the product is 5.95. Again, the known atomic weight of mercury is 200.6, and its specific heat 0.0335, and the product 6.7. Now the specific heat of calcium is 0.170, and the product 20×0.170 is equal to 3.4. But $2 \times 20 \times 0.170 = 6.8$. The value 2×20, or 40, for the atomic weight is therefore the correct one.

106. Exercises.

1. State the change which takes place in the total volume of the gases or vapors in each of the six actions mentioned in § 86.

2. If 1 liter of oxygen at 0° and 760 mm. weighs 1.429 g., what is the molecular weight (§§ 88, 101)?

3. Calculate the molecular weight of a gas, 200 c.c. of which at 0° and 760 mm. weigh 2.1 g. (§§ 88, 101).

4. Find the molecular weight of a gas, of which 250 c.c. at 18° and 752 mm. weigh 2.5 g. (§§ 88, 101).

5. The following are the weights of sulphur contained in the molecular weights of several of its compounds: 32.06, 64.12, 96.18. What is the atomic weight of sulphur (§§ 89, 92)?

6. What information is contained in each of the formulæ: CS_2, PCl_3, I_2, C_2H_2, C_2H_6 (§ 95)?

7. If two gases combine in the ratio 5 : 2 by volume, in what relative numbers do their molecules interact (§ 99)?

8. The density of sulphur dioxide is 0.00286. What is its molecular weight (§ 102)?

9. The density of a gas, air = 1, is 2.3. What is its molecular weight (§ 102)?

10. An element combines with hydrogen in the proportion 10.35 : 1, and its specific heat is 0.2. What is its atomic weight (§ 105)?

11. The molecular formula of a gas is CH_4. What is the gram-molecular weight? What volume does this weight occupy? What is the weight of 1 liter of the gas?

CHAPTER IX.

MAKING OF FORMULÆ AND EQUATIONS.

107. The formula (p. 65) is a condensed statement of the composition of a substance. Before we can make (*i.e.*, calculate) the formula for a substance, *we must* (1) *measure the proportions by weight of the constituent elements.* Then, *we must* (2) *express these proportions in multiples of the known atomic weights of the elements.*

108. Analysis and Synthesis. In the case of water H_2O we saw (p. 47) how the weights of hydrogen and of oxygen required to give a measured amount of water were determined. The composition of the water was found out by *putting the substance together* out of the elements. This method is called **synthesis** (Greek, *putting together*).

In the case of mercuric oxide we can take a weighed amount of the oxide, decompose it, and weigh the mercury formed. The difference is the weight of the oxygen. This process, of decomposing a substance to learn its composition, is called **analysis** (Greek, *decomposition*).

One or other — sometimes both — of these plans can be used with every compound.

Some of the results of such experiments have been given in the earlier chapters. For example:

Tin (100) + Oxygen (26.89) → Tin oxide (p. 11).
Lead (100) + Oxygen (7.72) → Lead oxide (p. 11).
Iron (100) + Oxygen (43) → Ferric oxide (p. 11).
Zinc (2.04) + Sulphur (1) → Zinc sulphide (p. 14).
Mercuric oxide (108) → Mercury (100) + Oxygen (8) (p. 24).

109. Making Formulæ. In the formulæ, these proportions are to be replaced by multiples of the atomic weights by whole numbers. We therefore divide the quantity of each element by the corresponding atomic weight. This operation gives us the factors by which the atomic weights are to be multiplied. The atomic weights we find in the table, where the values determined by the most expert chemists are collected.

For example. In the case of tin oxide the proportion of tin to oxygen is $\frac{100}{26.89}$. The atomic weights are 119 and 16 respectively. $100 \div 119 = 0.84$, and $26.89 \div 16 = 1.68$. The proportion $\frac{100}{26.89}$ now becomes $\frac{119 \times 0.84}{16 \times 1.68}$.

Now this proportion — like all chemical proportions — must be expressed in multiples of the atomic weight by *whole* numbers. Hence, we next find the greatest common measure of the two factors. It is 0.84. Indeed, in this simple instance, we can see that the ratio of the factors is 1 : 2. Dividing above and below by 0.84, we get $\frac{119 \times 1}{16 \times 2}$.

Now, the symbols stand for the atomic weights. Substituting these symbols, the proportion becomes $\frac{Sn \times 1}{O \times 2}$. The formula is therefore SnO_2.

Applying the same process to the lead oxide, we get

$$\frac{100}{7.72} = \frac{207.1 \times 0.483}{16 \times 0.483} = \frac{207.1 \times 1}{16 \times 1} = \frac{Pb \times 1}{O \times 1}, \text{ or PbO.}$$

Treating the other data in the same manner, we find: ferric oxide Fe_2O_3, zinc sulphide ZnS, and mercuric oxide HgO.

If the composition of the substance is given in percentages, the same process is used. Thus, the case of sodium sulphate works out as follows:

Elements.	Percentages.	At. wt.		Quotient.	÷	Formula.
Sodium.............	32.43	**23**	×	1.41	0.705	Na × 2
Sulphur.............	22.55	**32**	×	0.705	0.705	S
Oxygen.............	45.02	**16**	×	2.814	0.705	O × 4

The formula is therefore Na_2SO_4.

110. Making Equations. The condensed statements of chemical changes which we have been using can now be still further simplified by inserting the *formulæ* in place of the names of the substances (p. 75). Thus

$$Sn + O_2 \rightarrow SnO_2.$$

This is to be read: 119 parts (or 1 atomic weight) of tin, *acting chemically with* 2 × 16 parts (or two atomic weights) of oxygen, *give* 151 parts of stannic oxide. We may also read it thus: 1 atom of tin with 1 molecule of oxygen give 1 molecule of stannic oxide.

In making an equation there are **four stages or steps:**

1. Find out by experiment what the substances used and produced are.
2. Learn the molecular formula of each substance.
3. Set down the molecular formulæ in the form of a skeleton equation. Place the formulæ of the *initial substances* on the *left*, and those of the products on the right.
4. Adjust, or *balance* the equation.

For example:

(1) When hydrogen and oxygen combine, water is formed.

(2) The molecular formulæ are H_2, O_2, and H_2O.

(3) Skeleton equation: $H_2 + O_2 \rightarrow H_2O$.

(4) In accordance with the law of conservation of mass, the numbers of atomic weights (or atoms) of each element must be the same after the action as before it. Now the skeleton equation shows two atomic weights of oxygen before, and

thus far only one after the action, whereas there ought to be two then also. With O_2 (2 × 16 parts) we have enough oxygen to give $2H_2O$, which contains 2 × 16 parts of oxygen. But this will require us to take $2H_2$ to "balance" the equation. The final equation is, therefore:

Balanced Equation: $2H_2 + O_2 \rightarrow 2H_2O$.

Observe, we could not adjust the difficulty by writing $H_2 + O \rightarrow H_2O$, because each substance must be represented by its *molecular* formula, which stands for the weight of the substance in the standard volume of 22.4 liters, or one chemical unit weight, and in the case of oxygen this is O_2 (= 32 g.). Putting this in terms of the hypothesis, each formula must represent 1 molecule, and the molecules of oxygen contain 2 atoms. Hence we could not divide the oxygen molecule. But we *could take more than one molecule* of hydrogen, so we took 2 molecules of this substance.

The coefficients in front of formulæ multiply the *whole* formula. $2H_2O$ is equivalent to $2(H_2O)$, or two whole molecules of water.

111. Balancing Equations. Learning to balance equations correctly comes only by practice. Take, again, the case of iron rusting. The substances are iron (Fe), oxygen (O_2) and ferric oxide (Fe_2O_3). The skeleton equation is

$$Fe + O_2 \rightarrow Fe_2O_3.$$

We are not permitted to alter these formulæ themselves, but we may put coefficients in front of any of them to make the number of atomic weights alike on both sides. A good rule is *to pick out the largest formula and reason back from that.* Here, this is Fe_2O_3. To get the Os in *threes*, we must clearly take $3O_2$ (=6O). That will give us $2F_2O_3$. This, in turn, will require 4Fe:

Balanced: $4Fe + 3O_2 \rightarrow 2Fe_2O_3$.

112. Equations for Actions Already Studied. In the *preparation of oxygen* (p. 24) we used mercuric oxide and got mercury and oxygen:

Skeleton: $HgO \rightarrow Hg + O_2$.
Balanced: $2HgO \rightarrow 2Hg + O_2$.

Potassium chlorate has a composition shown by the formula $KClO_3$. It gives (p. 24) potassium chloride (KCl) and oxygen (O_2).

Skeleton: $KClO_3 \rightarrow KCl + O_2$.
Balanced: $2KClO_3 \rightarrow 2KCl + 3O_2$.

The variety of chemical change, where one substance gives two (or more) substances, *decomposition* (p. 20), is readily recognized in these equations.

Substances, like the manganese dioxide (catalytic agent) used here, and the water so often employed as a solvent, **when they undergo no chemical change, are omitted from the equation.** They are simply part of the apparatus.

When the water takes part in the action, however, it must, of course, be included. Thus sodium peroxide (Na_2O_2) and water (H_2O) interact (p. 26) to give sodium hydroxide and oxygen:

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2.$$

113. *The Preparation of Hydrogen* (p. 39) from sodium (Na) and water gives sodium hydroxide ($NaOH$) and hydrogen (H_2):

$$2Na + 2H_2O \rightarrow 2NaOH + H_2.$$

When steam is passed over iron (p. 39), we get hydrogen and magnetic oxide of iron (Fe_3O_4):

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2.$$

The liberation of hydrogen by the action of zinc (Zn) upon sulphuric acid (H_2SO_4), where the products (p. 41) are hydrogen and zinc sulphate, is shown thus:

$$Zn + H_2SO_4 \rightarrow H_2 + ZnSO_4.$$

Again, iron and hydrochloric acid (HCl) give hydrogen and ferrous chloride ($FeCl_2$):

$$Fe + 2HCl \rightarrow H_2 + FeCl_2.$$

In the last two equations the variety of chemical changes called *displacement* (p. 40), where one elementary substance displaces another from a compound, is well illustrated.

The equation for the *formation of water* by union of hydrogen and oxygen,

$$2H_2 + O_2 \rightarrow 2H_2O,$$

has already (p. 77) been discussed. The *reduction* of an oxide, such as magnetic oxide of iron or cupric oxide, by hydrogen (p. 46), gives the metal and water:

$$Fe_3O_4 + 4H_2 \rightleftarrows 3Fe + 4H_2O.$$
$$CuO + H_2 \rightarrow Cu + H_2O.$$

Upon examining these equations for reductions, we perceive that they are illustrations of displacement also.

114. *Reversible Actions* (p. 56), like the decomposition of water by heating, and the recombination of the elements on cooling (p. 54), are shown by using two arrows:

$$2H_2O \rightleftarrows 2H_2 + O_2.$$

The equation may be read from either end. The decomposition and formation of hydrates (p. 55) are also reversible actions. In the case of zinc sulphate, the equation is

$$ZnSO_4 + 7H_2O \rightleftarrows ZnSO_4{,}7H_2O.$$

115. Reaction Formulæ. In the foregoing formula for the hydrate of zinc sulphate, it will be seen that we do *not* add together all the atoms of oxygen, and write $ZnH_{14}SO_{11}$. The latter would show the composition of the substance correctly, but it would show *nothing more.* Now chemists find it convenient, frequently, to alter the formula so that it shall indicate also *some important* chemical property or *reaction* of the substance. Hence the formula $ZnSO_4, 7H_2O$, which indicates at a glance the relationship of the substance to zinc sulphate ($ZnSO_4$). The hydrate is *made from* zinc sulphate by adding water, and is easily *decomposed into* these two substances again. The reaction formula hints at this familiar *reaction*. Note, however, that the comma (,) does *not* indicate a *mixture* of the materials, such as $ZnSO_4$ and H_2O, but a single substance composed of both. The plus (+) sign is used between the formulæ of different, uncombined substances in a mixture.

In accordance with this plan, washing soda, hydrate of sodium carbonate (p. 55), is written $Na_2CO_3,10H_2O$, and bluestone (p. 55), hydrate of cupric sulphate, $CuSO_4, 5H_2O$.

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116. Dissociation. A decomposition which, like those in § 114, is *reversible* is called a **dissociation.** When heat is the agent producing the change, it is sometimes called a *thermal* dissociation. Not all decompositions are reversible. Thus potassium chlorate decomposes to give potassium chloride and oxygen, but these products will not combine under any known conditions, directly, to give potassium chlorate.

117. Molecular Formulæ. In this chapter, for the sake of simplicity, we have so far left in the background the fact that the formula must represent a molecular weight of the substance, as well as its composition. The total weight, for which the symbols in a formula stand, must be equal to the weight of the substance occupying the gram-molecular volume. In other words, the *formula-weight* must represent one cube-full (Fig. 29, p. 61) of the substance. This is true, as we have seen, of the formulæ H_2O and HCl (see § 119).

In the cases of tin oxide (SnO_2) and ferric oxide (Fe_2O_3), we have substances which cannot be converted into vapor or dissolved, so that their molecular weights are unknown. *In such cases,* as we have seen (p. 66, § 94), *we use the simplest formula* that will show the correct proportions.

118. Molecular Formulæ of Simple Substances. With oxygen (O_2) and hydrogen (H_2), however, the double formulæ are used, instead of the simpler O and H, because the weights 2 × 16 and 2 × 1.008 are the ones which fill the cube. The molecules of *all* elements are not diatomic, however. Thus the cube-full of mercury vapor weighs only 200.6, the same as the atomic weight, and the correct molecular formula of the element is therefore Hg. Similarly, the correct formulæ are Na (sodium), K (potassium), and Zn (zinc). But the weight of 22.4 liters requires us to write N_2 for nitrogen, P_4 for phosphorus vapor and S_2 for sulphur vapor (above 1000°). Hence equation (6) on p. 60 reads: $2Zn + S_2 \rightarrow 2ZnS$.

After all, there is nothing surprising in the fact that the molecules even of elementary substances should, in some cases, contain several atoms. All that it means, in the case of an element with diatomic molecules, such as oxygen ($O_2 = 32$), is that, when oxygen combines with another element, each molecule of oxygen will be divided between two molecules of the product if the latter contain only 16 parts of oxygen each.

119. Molecular Formulæ of Compounds. The need of attention to making our formulæ molecular comes out also in the cases of many compounds. Thus, formaldehyde (a disinfectant) has the composition CH_2O, and its molecular weight is 30, so that CH_2O ($= 12 + 2 + 16$) is the correct formula. But acetic acid (the sour substance in vinegar) has the same composition, CH_2O, only its molecular weight is 60, and the formula is therefore written $C_2H_4O_2$ ($= 24 + 4 + 32$).

For gaseous and volatile substances the correct molecular formulæ are always used. Thus, equation (5) on p. 60 is written:

$P_4 + 5O_2 \rightarrow P_4O_{10}$, because the molecular weight of phosphorus pentoxide is 284, and requires the formula P_4O_{10} rather than P_2O_5.

120. Warnings. Do not place the formulæ of the *products* upon the left, but upon the right-hand side of the equation.

Point the arrow towards the products.

Use the molecular formulæ for elementary substances (O_2, H_2, N_2, etc.). The molecular formulæ, when they are known, are the only ones given in the text. The *symbols*, as given in the table on the rear cover, must be made into molecular formulæ before use in equations.

121. Exercises.

1. Using the data given on p. 29, calculate the simplest formulæ of sulphur dioxide, phosphorus pentoxide, and carbon dioxide.

2. Using the results of 1, make and balance the equations for the union of each of the three elements, sulphur, phosphorus, and carbon, with oxygen.

3. Using the information on p. 29, make and balance the equations for the interaction with oxygen of: (a) carbon disulphide (CS_2), (b) zinc sulphide (zinc oxide is ZnO), and (c) wood (assuming the formula of the latter to be that of cellulose, $C_6H_{10}O_5$).

4. Make and balance the equations for the actions on water (p. 38) of: (a) potassium (giving KOH), and (b) calcium (giving CaO_2H_2, usually written $Ca(OH)_2$).

5. Using the data in regard to the action of zinc on hydrochloric acid, given on p. 41, calculate the formula of zinc chloride and make the equation.

6. Make equations for the action of magnesium and aluminium upon hydrochloric acid (giving $MgCl_2$ and $AlCl_3$) and of magnesium upon sulphuric acid (giving $MgSO_4$).

7. Make a molecular equation for the decomposition of hydrochloric acid by electrolysis (p. 43).

8. Make equations for the formation of the hydrates of sodium carbonate and of cupric sulphate (§ 115), by union of the anhydrous substances with water.

CHAPTER X.

SOLUTIONS.

122. The property that many substances have of dissolving in others is a most interesting and valuable one. The value lies chiefly in the fact that some substances are easily soluble in a given liquid and others are, practically, not soluble in it at all. These differences in solubility enable us to accomplish many things otherwise impossible. Thus, we separated sulphur from zinc (p. 12), by using carbon disulphide (CS_2) to dissolve the former. We must first learn precisely what is meant by a solution, and then we shall be ready to understand the uses and properties of solvents and solutions.

123. Solution. We distinguish carefully between a solution and a mere mixture.

In a solution the dissolved substance is so completely spread throughout the solvent (such as water) *that it gives no evidence to the eye of its presence.* The only exception to this is when the substance is colored, and confers a general tint on the whole solution. Furthermore, *the dissolved substance never settles out,* no matter how long we wait.

On the other hand, when the liquid is dull, or cloudy, or muddy, the liquid is a mixture. The substance is simply suspended, not dissolved, and will eventually settle out. Sand, shaken with water, settles at once. Flour, mixed with water, settles more slowly. Filtration (p. 12) quickly separates the flour, which remains on the paper, from the water, which runs through. These are not dissolved, but *suspended* substances.

Milk owes its whiteness chiefly to minute drops of oily matter which reflect much light from their surfaces. They pass easily through filter paper. But they slowly rise to the top, being lighter than water, and are likewise not dissolved, but suspended. A mixture of two *liquids*, like milk, is called an **emulsion.**

Chemists commonly call the dissolved body the **solute.** Gases, liquids, and solids may all be solutes, and dissolve in suitable solvents.

124. Solvents. Water is by far the commonest and most useful solvent. Very many inorganic substances dissolve in it easily. The fact that many (like zinc and sand) do not, enables us to separate the components of a mixture containing a soluble and an insoluble substance.

Many organic substances, such as fats, paraffin, petroleum, tar, rubber, cotton, paper, shellac, and so forth, do not dissolve to any measurable extent in water. But fats dissolve readily in ether ($C_4H_{10}O$), in carbon disulphide (CS_2), in carbon tetrachloride (CCl_4), and in chloroform ($CHCl_3$). For this reason these substances remove grease which has accidentally got into cloth. Paraffin, petroleum, and tar dissolve in gasoline (petrol), and in benzene (C_6H_6). Cotton and pure paper (like filter paper) will dissolve in strong sulphuric acid. Alcohol (C_2H_6O) dissolves shellac (to make varnish).

Again, water will not dissolve carbon disulphide, chloroform, carbon tetrachloride, gasoline or benzene. But it dissolves alcohol in any amount, and ether in limited quantity. Some organic substances, like sugar, dissolve easily in water, but hardly at all in the other solvents just mentioned. Hence candy or molasses can be taken out of cloth by water, but not by solvents for fats.

Chemists have as yet found no explanation of these striking differences in solubility.

125. Saturation. As a rule, not more than a certain amount of a solute is dissolved by a given quantity of the solvent. By shaking the solute with the solvent for a sufficient length of time, this maximum amount will finally be dissolved. The solvent is then said to be **saturated** by the solute in question. Thus, 100 c.c. of water at the ordinary temperature will dissolve as much as 5 g. of potassium chlorate, but not more. The 100 c.c. of water will dissolve 90 g. of Epsom salt, however, before the solvent becomes saturated. On the other hand, a saturated solution of chalk (calcium carbonate) in water will contain only 0.0013 g. in 100 c.c.

To describe these cases we should say that potassium chlorate is only moderately soluble in water, Epsom salt very soluble, and chalk **insoluble.** But no substance is *absolutely* insoluble.

The number of grams of the solute required to saturate 100 c.c. of the solvent we call the **solubility** of the substance (at the existing temperature). Examples are given in § 127.

In some cases there is no limit to the solubility, and therefore no possibility of the solution reaching saturation. Thus alcohol or glycerine and water will mix in any proportion. Such pairs of substances are said to be **miscible in all proportions.**

126. Dilute and Concentrated Solutions. A **dilute** solution is one containing little dissolved matter, whether the matter is naturally very soluble or not. A **concentrated** solution is one containing much of the dissolved substance, and such a solution can be made with very soluble solutes only.

127. Temperature and Solubility. The solubility of every substance in any solvent varies more or less with the temperature. The solubility of niter (potassium nitrate KNO_3) in water shows great variation, namely 13 g. in 100 c.c. at 0°, 26 g. at 20°, 140 g. at 70°. On the other hand, the solubility of common salt (sodium chloride NaCl) is more constant, 35.5 g. at 0°, 36.5 g. at 20°, 38 g. at 70°, 40 g. at 100°.

Usually, as in these two cases, the solubility *increases* with rise in temperature, but often it diminishes. Thus, the solubility of slaked lime (calcium hydroxide $Ca(OH)_2$, used to make lime water) is 0.175 g. at 20° and 0.079 g. at 100°, and that of anhydrous sodium sulphate (Na_2SO_4), 55 g. at 32.5° and 42 g. at 100°.

The solubility of gases usually diminishes with rising temperature. This may be shown by heating cold tap-water in a beaker. The dissolved gases, originally obtained from the air, appear in bubbles on the bottom and sides as the temperature rises.

128. Crystallization. If the solvent has been saturated while warm, and substance is one that is less soluble at lower temperatures, then, when the temperature falls, the solute begins to come out of solution. The amount appearing, of course, is only the **excess** beyond what is needed to saturate the solvent at the lower temperature.

If the solute is liquid at the new temperature, it appears at first as a cloud of drops, rendering the liquid milky. This may be shown by cooling a hot, aqueous solution of phenol (carbolic acid).

If the solute is solid, then the particles, as they appear, take the form of **crystals** (Figs. 30–34). These *grow* by taking on more of the separating solute. If the cooling goes on slowly, very large crystals can finally be obtained. On the other hand, with rapid cooling, new crystals are continually formed, and a fine, crystal-meal falls to the bottom of the solution. The crystals in this meal, however, when viewed through a lens, are seen to be just as perfect as the larger ones.

When a dilute solution is used, instead of a saturated one, crystals may still be obtained. A *part* of the solvent must first *be removed,* however. This may be done, either by boiling the solution for some time, or by leaving it to evaporate in a wide dish in which a large surface is exposed.

When the dissolved substance can form a hydrate (p. 54) which is stable at the temperature of crystallization, the crystals are composed of this hydrate.

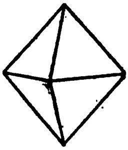

Fig. 30
Octahedron
(Alum)

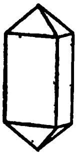

Fig. 31
Square Prismatic

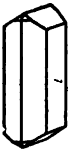

Fig. 32
Rhombic
(Niter)

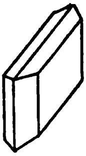

Fig. 33
Monosymmetric
(Gypsum)

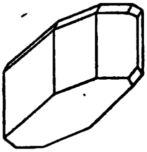

Fig. 34
Asymmetric
(Hydrated cupric sulphate)

The *whole* of the solvent may be boiled off. But in this case, good crystals of the solute are never obtained — the residue is usually a crust composed of imperfect crystals.

When the substance is more soluble in cold than in hot water, then crystallization is produced by raising the temperature.

129. Crystallization from a Melted Mass. In this connection, it should be noted that there is another way of obtaining crystals. This is to *melt* the substance (without any solvent), and allow the mass to cool slowly. When a part has solidified, the rest of the liquid is rapidly poured off. Metals and many other fusible substances give good crystals in this way. Water itself, when it freezes, deposits radiating, hexagonal crystals of ice.

130. Supersaturation. When a hot, saturated solution is cooled, there is quite commonly some delay before the crystals begin to appear. The solution, pending the appearance of the crystals, is then said to be **supersaturated.** In most cases the crystals appear in due course, especially if the liquid is stirred. But certain substances have a tendency to remain indefinitely in the state of supersaturated solution. The hydrates of sodium sulphate (Na_2SO_4, $10H_2O$) and of sodium thiosulphate (photographers' "hypo" $Na_2S_2O_3$, $4H_2O$) are of this nature. The addition of a minute crystal of the substance concerned ("inoculation"), however, always starts the crystallization (Fig. 35).

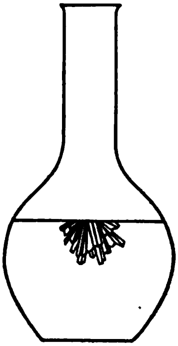

Fig. 35

131. Heat of Solution. Most substances absorb heat when they dissolve, making the solvent cooler, and give out heat when they crystallize. Thus, in the two cases last mentioned, when the crystallization is brought about in the cool, supersaturated solutions, the rise in temperature is considerable.

This fact has been utilized in devising a sort of hot-water bottles. Each is a rubber bag containing a supersaturated solution of sodium acetate. Whenever the heat is wanted, the stopper is taken out, rubbed with the finger, and screwed back. This spreads on the inner surface of the stopper, next the liquid, some of the crystals adhering to the screw, and so starts the crystallization. The bottle then becomes warm. After being thus used, the bag is placed, without being opened, in boiling water to redissolve the crystals, and, when cold, is ready for use again.

132. Influence of the Solute upon the Solvent. The dissolving of a substance alters the properties of the solvent. The observed changes may be divided into two classes.

In one of these two classes equal numbers of dissolved molecules of different substances produce the *same* amount of change. The effect appears thus to be due largely to mechanical causes. Of this nature are the lowering in the vapor pressure of the liquid (§ 133), the raising in its boiling-point (§ 134), and the lowering in its freezing-point (§ 135).

In the other class, the amount of the change varies with the substance dissolved. Very striking and difficult to explain, for example, are the erratic changes in volume which occur when solution takes place. Effects of this class show that chemical changes often accompany solution. Thus, 58.5 g. of salt (volume 27.5 c.c.) and 10,000 c.c. of water have a volume totalling 10,027.5 c.c., but, when they are dissolved, the solution measures only 10,016.5 c.c. This is a very dilute solution (about 1/2 per cent), so that the contraction of 11 c.c. is relatively considerable. In a 20 per cent solution of salt, the shrinkage is 26.7 c.c. per liter, or about twenty-four times as great. On the other hand, 214 g. of ammonium chloride (volume 142.5 c.c.) and 843.5 c.c. of water have a total volume of 986 c.c., but when dissolved give 1000 c.c. of solution. Here there is an *expansion* of 14 c.c. In the case of table-sugar and water, however, there is almost no change in volume.

133. Vapor Pressure of Solutions. A non-volatile solute tends to diminish the vapor pressure of the solvent. Hence aqueous solutions have *lower* vapor pressures than has the pure solvent (water).

If the solution is very concentrated, and the lowering in the vapor pressure very great, the solution may give a vapor pressure of water less than that commonly present in the atmosphere. Such a solution, placed in an open vessel, will not evaporate. On the contrary, it will take up moisture from the air and increase in bulk. For this reason very soluble substances are commonly moist and, when exposed to the air, extract water from the latter and dissolve in this water. This behavior is called **deliquescence,** and is shown, for example, by the hydrate of calcium chloride $CaCl_2, 2H_2O$, used to dry gases (p. 48).

134. Boiling-Points of Solutions. Since the solute interferes with the liberation of vapor, it naturally makes the solution more difficult to boil than the pure solvent. It *raises the boiling-point* to a higher temperature.

It was shown by Raoult (1886), that, in dilute solutions, equal numbers of molecules of different solutes raise the boiling-point of a given solvent to the same extent.* Thus, one molecular weight of sugar ($C_{12}H_{22}O_{11}$ = 342 g.) or of glycerine ($C_3H_8O_3$ = 92 g.), dissolved in 1000 c.c. (1 liter) of water, will each raise the boiling-point from 100° to 100.52°.

Molecular weights of non-volatile substances can be measured by simply finding out what weight of the substance, when dissolved in 1000 c.c., is required to raise the boiling-point of water from 100° to 100.52°.

135. Freezing-Points of Solutions. The presence of the solute similarly tends to prevent the *freezing* of the solution, for freezing means the separation of a part of the *pure solvent* in the form of ice. Hence solutions can be frozen only at temperatures *below* those of the pure solvents. Thus, one molecular weight of a substance,* such as sugar (342 g.) or glycerine (92 g.), dissolved in 1000 c.c. of water, will cause the water to freeze at −1.86° instead of 0°. Molecular weights can be measured by this method also.

This behavior explains why sea water is much less often frozen in cold weather than fresh water.

It explains also *why salt thrown on ice will cause the latter to melt.* Saturated salt solution freezes only at −21° (−6° F.),

---

* For important exceptions, see § 204.

to give a mixture of pure ice and pure salt, both in solid form. Hence, ice and salt can not permanently exist together *above* that temperature. When the outside temperature is below −6° F., salt will no longer melt the ice. But calcium chloride, which is more soluble, will do so. A mixture of ice and salt, giving the temperature −21°, is called a **freezing mixture.** Such a mixture is used in freezing ice cream and ices.

136. Is Dissolving a Physical or a Chemical Change? This is a question still much discussed amongst chemists. Probably in simple, typical cases, like dissolving paraffin in gasoline or benzene, the cohesion may be considered purely physical, and the solution contains *both* components in unchanged chemical condition.

On the other hand, when water is used, as it is more frequently than any other solvent, chemical changes undoubtedly take place. The water itself, at least, is always changed. It is composed chiefly of molecules of dihydrol $(H_2O)_2$, with some trihydrol $(H_2O)_3$ near to 0°, and increasing amounts of monohydrol H_2O at higher temperatures. Dissolving *any* substance in water must upset the equilibrium amongst these different kinds of molecules:

$$(H_2O)_2 \rightleftarrows 2H_2O$$

and produce more of one and less of the other kind. This is the extent of the chemical change in the water.

The dissolved substance probably does not always combine with any of the water. But there is evidence that, in many cases, it does. The nature of the compounds is hard to determine, and no simple statement can as yet be made about them. But the compounds, whatever they are, are physically dissolved in the rest of the water.

Dissolving, therefore, is partly a chemical, and only partly a purely physical process.

137. Exercises.

1. Give two ways of separating a mixture, consisting of a suspended solid and a liquid (p. 12).

2. If you had a spot on your clothing consisting of: (a) grease, (b) sugar, or (c) sugar and grease together, or (d) varnish, how should you proceed in each case to remove the spot?

3. If chalk (5 g.) and potassium chlorate (5 g.) were mixed, how should you separate them (p. 86)? Explain how you could secure each substance in its original, dry condition (pp. 87–8). How much of the chalk would necessarily be lost in the process?

4. Could you make (a) a concentrated, (b) a saturated solution of chalk in water (p. 86)? Of alcohol in water?

5. If you saturated 200 c.c. of water at 70° with (a) salt, or (b) potassium nitrate, and then cooled the clear liquid to 20°, what weight of the solid substance would separate out in each case (§ 127)?

6. To make as concentrated a solution of lime water as possible, should you use hot water or cold (p. 87)?

7. Explain why boiled water has a slightly different taste from tap-water that has not been boiled (p. 87).

8. Explain why potassium carbonate becomes wet, and finally dissolves, when exposed to moist air (p. 90). How must calcium chloride be preserved from becoming moist?

9. If 52 g. of a substance dissolved in 1000 c.c. of water gives a solution boiling at 100.26°, what is the molecular weight of the substance (p. 91)?

10. If 68.5 g. of a substance, dissolved in 500 c.c. of water, gives a solution freezing at −1.86°, what is the molecular weight of the substance (p. 91)?

11. How much glycerine ($C_3H_8O_3$) could you dissolve in 1 liter of water, and still be able to freeze the water with ice and salt (p. 91)?

12. Explain why an "acetate" hot-water bottle can be used over and over again. What is the source of the heat it gives out each time it is used?

CHAPTER XI.

HYDROCHLORIC ACID. CALCULATIONS.

138. Thus far, the substances we have studied have been mainly air and its components and water and its constituents. Another of the simpler, familiar substances, **common salt** or sodium chloride ($NaCl$) may now be taken up. Large amounts of it are used in the household, in cooking and in making freezing mixtures. Still larger quantities are consumed in manufacturing washing soda and soap, for both of which it supplies the necessary sodium. It is employed also to furnish the chlorine for bleaching materials. We shall consider it first as a means of making compounds of chlorine.

139. Preparation of Hydrogen Chloride. When a few drops of commercial, concentrated sulphuric acid (H_2SO_4) are poured upon common salt in an open dish, vigorous effervescence begins. This indicates that a gas is forming bubbles upon the salt and that the bubbles are rising through the layer of acid and bursting. The gas is itself invisible, but when we breathe upon the contents of the vessel, a heavy fog is produced. This is due to condensation of water vapor (in the breath) to droplets of water, in which the gas has dissolved. The fog is composed, in fact, of drops of a solution of hydrogen chloride (HCl) in water, which receives the name of **hydrochloric acid** (in commerce, muriatic acid).

In order to handle the gas more readily, the sulphuric acid may be allowed to fall from a funnel, drop by drop, upon salt contained in a flask (Fig. 36). Soon the air in the flask is all displaced by the gas, and the latter issues from the open, delivery tube. If a U-tube containing some water is attached to the delivery tube, the gas dissolves in the water as fast as it is formed.

If the correct proportions of the materials are used, then, when the action is over, all that remains in the flask is a white solid, different from salt, and called sodium-hydrogen sulphate $NaHSO_4$. A part of this may be in solution in a little water, contained originally in the commercial sulphuric acid, of which water commonly forms from 6 to 7 per cent. The equation is easy to make from the formulæ given,

$$NaCl + H_2SO_4 \rightleftarrows HCl\uparrow + NaHSO_4,$$

and requires no further balancing.

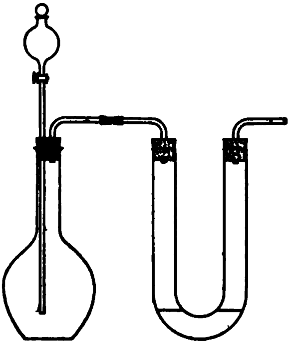

Fig. 36

140. Other Sources of Hydrogen Chloride. Chlorides of other metals could be substituted for the sodium chloride in this action, and all but the less soluble ones would give hydrogen chloride freely. Common salt is employed because it is the cheapest of the chlorides.

While theoretically any acid would, like sulphuric acid, furnish the required hydrogen, and liberate hydrogen chloride, yet in practice no other acid works so well. Some, like phosphoric acid H_3PO_4, act too slowly, because they do not dissolve sodium chloride so readily. Others, like hydrofluoric acid HF, are too volatile, and the heat of the action would send them over with the hydrogen chloride in the form of vapor. Sulphuric acid, itself, does not boil below 330°. Others, like nitric acid HNO_3, would react chemically with hydrogen chloride. Still others, like hydriodic acid HI, being gases, could be used only in aqueous solution, and the water would dissolve the hydrogen chloride produced, and prevent its escape from the vessel. Aside from these objections, all the other acids are more expensive than sulphuric acid.

It must be noted that the liberation of hydrogen chloride by sulphuric acid does not show the latter to be the more active acid. The opposite is really the case. The action is reversible (§ 83). But the sulphuric acid is not volatile, and remains in the flask to continue its action, while the hydrogen chloride is a gas, and leaves the interacting mixture in gaseous form. The last fact is indicated by the **arrow**, pointed **upwards,** in the equation.

141. Physical Properties. Hydrogen chloride is a *colorless* gas. It is sour in *taste*, and has a sharp *odor*. Breathing even a very little causes coughing. It is irritating, but not poisonous in small amounts.

The gas is exceedingly *soluble* in water, one volume of which, at 15°, will dissolve no less than 455 volumes of the gas. The saturated solution at 15° contains nearly 43 per cent of the gas by weight. The concentrated hydrochloric acid of commerce contains about 35 per cent.

The *density* of the gas (weight of 1 c.c.) is 0.001628. Of more interest to the chemist is the weight of 22,400 c.c. or 22.4 liters (the gram-molecular volume), namely 36.468 grams. This is the molecular weight of the substance. As we have seen (p. 61), it is made up of 1.008 g. of hydrogen combined with 35.46 g. of chlorine.

Is the gas heavier or lighter than air? This question is answered at once if we recall the fact that the 22.4-liter cube-full of air weighs 28.95 g. (p. 71). This gas is one-fourth heavier.

The gas can be *liquefied* by pressure alone at any temperature below 52° (its critical temperature). One atmosphere pressure will liquefy it at −84°, which is therefore the boiling-point of liquefied hydrogen chloride.

142. The Liquefiability of Gases. It will help us to remember which gases are hard to liquefy and which easy, if we memorize the fact that Faraday (from 1823 to 1845) liquefied most of the familiar gases, and failed only with *three, which are the difficult cases*, namely, *hydrogen*, *oxygen*, and *nitrogen*. *Nitric oxide* NO and *carbon monoxide* CO are also difficult to liquefy. The *six "inert" gases* (§§ 313–5) were not known in his time, and these must now be added to the difficult class.

143. Chemical Properties. In the case of a *compound*, the chemical property in regard to which we first inquire is its **stability.** Is it easy or difficult to decompose by heating? Hydrogen chloride can be heated to 1800° before even a trace of it is dissociated into hydrogen and chlorine. It is, therefore, *very stable.*

When hydrogen chloride is mixed with *ammonia* gas, as the latter rises, for example, from aqueous ammonia, a direct combination takes place. The gases *unite* to form a cloud of fine, solid particles of ammonium chloride.

$$HCl + NH_3 \rightarrow NH_4Cl.$$

144. Some Chemical Properties of the Solution. The chemical properties of the aqueous solution, hydrochloric acid, are especially interesting. The solution is *sour in taste.* This property is shown by all acids which are soluble in water.

With certain organic compounds it gives new compounds possessing a very characteristic color, and the appearance of this color is used as a *test.* Thus **azolitmin**, contained in **litmus** (an extract from certain lichens), is deep violet-blue in color. When a drop of even very dilute hydrochloric acid is added to litmus solution, the azolitmin changes into a bright red substance. This effect is produced by all soluble acids.

Often strips of filter paper, dipped in litmus solution and dried (**litmus-paper**) are used. When dipped in the acid they turn pink.

Certain metals, namely those above hydrogen in the order of activity (p. 42), when placed in hydrochloric acid, *displace* and liberate *hydrogen* gas. The same metals, as we have seen (p. 42), liberate hydrogen from all soluble acids.

Hydrochloric acid interacts with many *compounds* in solution. In some instances, as, for example, when the acid is added to a solution of silver nitrate ($AgNO_3$, lunar caustic), one of the new substances produced can be seen, because it appears as a precipitate (see § 145, below). The precipitate is silver chloride ($AgCl$), and is white and curdy in appearance. The other product, nitric acid (HNO_3), remains dissolved and invisible:

$$HCl + AgNO_3 \rightarrow AgCl \downarrow + HNO_3.$$

The **downward arrow** indicates the precipitate. This sort of action, whether it gives a precipitate or not, is always a double decomposition (see § 146, below). Such double decompositions are produced by all acids, although the products, unless they are insoluble, are not visible.

If we look back at these four properties of the solution, we see that they are properties common to all acids. If, therefore, we sum up, by saying that in solution hydrogen chloride *is an acid*, we have given in one word the important properties of the solution.

145. Precipitation. When two soluble substances, which are capable of acting chemically upon one another, are dissolved, and the solutions are mixed, the action takes place between the dissolved materials. If one of the products is not soluble, then a *supersaturated solution* (p. 89) *of this product is at once produced.* As a rule, this substance then becomes visible as a fine powder, called a **precipitate,** suspended in the liquid.

Often the precipitated product can be recognized by the physical *appearance* of the precipitate, and so this sort of action is used as a test for one of the *original* substances. Thus, precipitates are classified according to their color. Again, precipitates of the same color differ in physical appearance, and may be described as **gelatinous, curdy, pulverulent,** or **crystalline.** In the two former cases, at least, the precipitation is so sudden that there is not time for crystals to be formed, and the product is **amorphous** (Greek, *without form*).

146. Double Decomposition. In this chapter we meet for the first time with another variety of chemical change. If we examine the equation for the action of silver nitrate on hydrochloric acid (p. 98), we shall see that the silver nitrate decomposed as if it had been made up of two parts, namely (Ag) and (NO_3). The hydrochloric acid similarly separated into its two parts (H) and (Cl). The (Ag) then united with the (Cl) and the (H) with the (NO_3).

$$(Ag)\ (NO_3) + (H)\ (Cl) \rightarrow (Ag)\ (Cl) + (H)\ (NO_3).$$

Since both original substances decomposed, this whole change is called a **double decomposition** (§ 202). A sort of exchange between the halves of the decomposing substances took place.

The hydrogen chloride was prepared by an action (p. 95), which, if we write it as follows, is seen to be of the same class:

$$(Na)\ (Cl) + (H)\ (HSO_4) \rightarrow (H)\ (Cl) + (Na)\ (HSO_4).$$

147. The Varieties of Chemical Change. Almost all chemical changes belong to one or other of the varieties we have already met with and defined (§§ 16, 33, 59, 146). These, along with one example of each, are now placed together:

1. **Combination:** $Zn + S \rightarrow ZnS$.
2. **Decomposition:** $2KClO_3 \rightarrow 2KCl + 3O_2$.
3. **Displacement:** $Zn + H_2SO_4 \rightarrow H_2 + ZnSO_4$.
4. **Double Decomposition:** $AgNO_3 + HCl \rightarrow AgCl + HNO_3$.

In the first, *2* (*or more*) *substances* give *1 substance.*
In the second, *1 substance* gives *2* (*or more*) *substances.*
In the third, *1 element* and *1 compound* give *1 element* and *1 compound.*
In the fourth, *2 compounds* give *2 compounds.*

5. The actions *not* included above are those where *one substance* gives *one* (different) *substance.* This kind of change is called **internal rearrangement.** We shall meet with very few examples of it.

This classification suffices for most purposes. But, for special kinds of cases, some other names are used. Thus, a **dissociation** (p. 81) is an action which belongs to *both* of the first two classes, because it is *reversible.* For example,

$$2H_2O \rightleftarrows 2H_2 + O_2.$$

Again **oxidation** (p. 29) and **reduction** (p. 46) are connected with the particular substances, such as oxygen, which are concerned in the action. The first classification (Nos. 1 to 5) paid no attention to the kinds of elements which were present. Thus, every decomposition is a decomposition. If it is reversible, then it is *also* a dissociation. If oxygen is set free, then it is a reduction *as well.*

148. Uses of Hydrochloric Acid. This substance is used as a source of chlorine. It is employed for cleaning metals. Although present in very small proportions (about 1 part in 500) in the gastric juice of the stomach, it is a most important component of this fluid. It is sometimes given as a medicine, when the natural supply is too small.

CALCULATIONS.

149. Calculations Connected with Formulæ. In previous chapters (pp. 65, 76) we have seen that formulæ represent the composition of substances, and we have seen how the formula of each substance is worked out from the data obtained by experiment. Some ways in which the information contained in formulæ can be used may now be taken up.

150. The Composition from the Formula. Take, for example, the formula for silver nitrate, $AgNO_3$. To learn the composition of this compound, we look up the atomic weights (see rear cover of this book). We find Ag = 107.88 parts of silver, N = 14.0 parts of nitrogen, $O_3 = 3 \times 16.0$ or 48.0 parts of oxygen. The proportions of the constituents, in the same order, therefore, are 107.82 : 14 : 48.

What is the proportion of nitrogen to oxygen alone? It is 14 : 48, or, dividing by 14, it is 1 : 3.43

151. Significant Figures. The division of 14 into 48 really gives the quotient $3.\dot{4}2857\dot{1}$. But no atomic weights have been measured so accurately that we know the values of the numbers beyond the *second* place of decimals, or (usually) four figures in all. Hence *3.43 is just as likely to be the exact value as the longer number*. In the most exact calculations we round the number off at the second decimal. For rougher purposes we round it off at the first decimal.

152. The Formula-Weight. The sum of the weights of the constituents indicated in the formula is called the **formula-weight.** For silver nitrate this has the value, 107.88 + 14.0 + 48.0, or 169.88.

If the substance is a gas, or is easily volatile, the formula-weight will be also the *molecular weight*. Thus, acetylene gas (used in lighting) has the formula C_2H_2. The composition is

$C_2 = 2 \times 12$ or 24 parts of carbon and $H_2 = 2 \times 1.008$ or 2.016 parts of hydrogen. The molecular weight is $24 + 2.016 = 26.016$. Again, hydrogen peroxide (used in medicine), a liquid, is decomposed when boiled, but it dissolves in water and depresses the freezing-point. Its molecular weight has therefore been determined (§ 135) and is H_2O_2. The molecular weight on which this formula is based is $2.016 + 32$, or 34.016.

When the substance is neither volatile nor soluble, the simplest formula is always used, and therefore only the formula-weight can be ascertained.

153. To Find the Percentage Composition. In silver nitrate the proportions are 107.88 of silver, 14.0 of nitrogen, and 48.0 of oxygen in a total of 169.88. *In one hundred* parts, the silver will be $\frac{107.88}{169.88} \times 100$, or 63.50; the nitrogen $\frac{14}{169.88} \times 100$, or 8.24, and the oxygen $\frac{48}{169.88} \times 100 = 28.25$.

The same results may be obtained by the rule of proportion. Thus, for the silver, $169.88 : 107.88 :: 100 : x$ where x is the percentage of silver.

154. Calculations by Use of Equations. We frequently desire to know what weight of a product can be obtained from a given weight of the necessary materials. For example, what weight of zinc sulphide can be made with 100 g. of sulphur? It is understood, of course, that the necessary zinc is available.

In such calculations mistakes are easily made. *The following* **rules** *must be strictly followed:*

First, write down the equation:

$$Zn + S \rightarrow ZnS.$$

Second, place beneath each formula the weight for which it stands:

$$\begin{array}{ccccc} \mathrm{Zn} & + & \mathrm{S} & \rightarrow & \mathrm{ZnS} \\ 65.37 & & 32.07 & & 97.44 \end{array}$$

Third, read the whole statement. In this case it reads: 65.37 parts by weight of zinc combine with 32.07 parts of sulphur to give 97.44 parts of zinc sulphide.

Fourth, re-read the original problem. Then place the amount given in the problem (100 g. of sulphur) under the formula of the substance concerned. Then observe that the problem asks "What weight of zinc sulphide?" and place an interrogation point or an x under the formula of *that* substance:

$$\begin{array}{ccccc} \mathrm{Zn} & + & \mathrm{S} & \rightarrow & \mathrm{ZnS} \\ 65.37 & & 32.07 & & 97.44 \\ & & 100 & & ?\ \text{or}\ x \end{array}$$

Fifth, read the problem as it now appears in this expanded equation: 32.07 g. of sulphur will give 97.44 g. of zinc sulphide, therefore 100 g. of sulphur will give x g. of zinc sulphide.

Sixth. The answer may be now obtained by stating the proportion in the *same order* (or as in § 155):

$$32.07 : 97.44 :: 100 : x\ (= 303.8\ \text{g.}).$$

If the expanded equation has been prepared correctly, this final statement is purely mechanical. It will be seen that only two of the three quantities in the expanded equation were really used.

155. Alternative to the Sixth Step. We may also say: If 32.07 g. of sulphur will give 97.44 g. of zinc sulphide, 1 g. of sulphur will give $\frac{97.44}{32.07}$ g. ($=3.038$ g.) of zinc sulphide. Then, if 1 g. of sulphur gives 3.038 g. of zinc sulphide, the 100 g. of sulphur will give 100×3.038 g. ($= 303.8$ g.) of zinc sulphide.

156. Warnings. In solving the exercises at the end of the chapter, beware of *three kinds of mistakes* commonly made by beginners.

1. Conquer a tendency to say that the symbols Zn and S stand for "1 part" of zinc or of sulphur. They stand for 1 *chemical unit*, or atomic weight, or atom, in each case, — that is to say for "65.37 parts" and "32.07 parts," respectively.

2. Follow the rules laid down above. When one has once *become familiar* with the art of solving such problems, running through the rules takes only a few seconds. The chemist does it almost unconsciously. The beginner *always* thinks he can ignore these rules, and he fails in consequence. Writing the equation in the expanded form, and then reading the problem into it are absolutely essential steps.

3. Do not read the original problem carelessly and make the equation *backwards*, that is, with the sides reversed. If there seems to be confusion somewhere, when the last steps are reached, this hint will probably show the cause of the difficulty.

157. Another Example. What weight of hydrogen is required to reduce 45 g. of magnetic oxide of iron to metallic iron?

Following the rules, as before, we reach the expanded equation:

$$\begin{array}{ccccccc}
Fe_3O_4 & + & 4H_2 & \rightarrow & 3Fe & + & 4H_2O. \\
3 \times 55.84 + 4 \times 16 & & 8 \times 1.008 & & 3 \times 55.84 & & 4(2 \times 1.008 + 16) \\
167.52 + 64 & & 8.064 & & 167.52 & & 4 \times 18.016 \\
231.52 & & 8.064 & & 167.52 & & 72.064 \\
45 \text{ g.} & & x & & & &
\end{array}$$

Observe that the atomic weights are multiplied by the subnumbers, so that, for example, $Fe_3 = 3 \times 55.84$. Observe also that the formula-weights are multiplied by the coefficients, when such occur, in front of the formulæ, so that, for example, $4H_2O = 4 \times 18.016$.

The proportion 231.52 : 8.064 :: 45 : x (= 1.57) supplies the answer, 1.57 grams of hydrogen.

Using the **alternative plan** (§ 155): If 231.52 g. of magnetic oxide are reduced by 8.064 g. of hydrogen, 1 g. will be reduced by $\frac{8.064}{231.52}$ g. (= 0.035 g.) of hydrogen. Hence, if 1 g. of magnetic oxide is reduced by 0.035 g. of hydrogen, 45 g. will be reduced by 45 × 0.035 g. (= 1.57 g.) of hydrogen.

158. Exercises.

write 10 – $\overset{29}{\text{nine}}$ ·17

1. Complete the equation $ZnCl_2 + H_2SO_4 \rightarrow ZnSO_4 +$, and attach the name of the substance to each formula in it.

2. Point out the differences in physical properties between oxygen and hydrogen chloride.

3. Make equations for the displacement of hydrogen from hydrochloric acid by zinc and by sodium (pp. 41 and 94).

4. Give additional examples of the first four varieties of chemical change (p. 100).

5. Classify (p. 100) the following actions: (a) the action of steam on iron (p. 79); (b) the rusting of iron; (c) the electrolysis of dilute hydrochloric acid (p. 44); (d) the effect of heating the hydrate of cupric sulphate (p. 55).

6. Is the decomposition of mercuric oxide a case of: (a) dissociation, or (b) oxidation or reduction?

7. What is the proportion of: (a) sodium to one part of chlorine in salt; (b) one part of hydrogen to nitrogen in nitric acid (§ 15)?

8. Calculate the percentage composition of: (a) sulphuric acid; (b) acetylene C_2H_2.

9. What weight of hydrogen is displaced by the action of 100 g. of zinc upon an excess of hydrochloric acid ($ZnCl_2$ is formed)?

10. What weight of silver chloride is formed by the interaction of 5 g. of sodium chloride with silver nitrate?

11. What should be the difference in cost of 1000 g. of oxygen according as it is obtained by decomposing mercuric oxide at $3.00 (12/6) per kilog. or potassium chlorate at 30 cents (1/3) per kilog.?

CHAPTER XII.

CHLORINE. CALCULATIONS.

159. Chlorine was discovered by Scheele (1774). It was supposed to be a compound containing oxygen, until the contrary was proved by Davy (1809–1818). It is used in immense quantities for making bleaching agents.

160. Occurrence. Many compounds of chlorine occur in nature, but the most plentiful is common salt (NaCl). Most of the matter dissolved in sea water is sodium chloride. Salt also occurs underground, either in strata in almost pure form, or mixed with rocky material. Near such deposits, wells and springs of salt water are common.

161. Preparation by Electrolysis of a Chloride. Chlorine is liberated by passing a current of electricity through an aqueous solution of a chloride, such as hydrogen chloride or sodium chloride (see Fig. 18, p. 43). Much of it is, in fact, manufactured by electrolyzing natural brines. The chlorine is liberated, first in solution and later as a gas, at the *positive* wire (anode).

162. Other Products of Electrolysis of Chlorides. In electrolyzing hydrochloric acid, the hydrogen is set free at the negative wire (cathode). With sodium chloride we might expect to get free sodium. It will be recalled, however, that sodium is very much more active than is hydrogen, and indeed displaces hydrogen from water. Hence the electrical energy *sets free the more easily liberated element* — the hydrogen — and the sodium remains in the solution as sodium hydroxide (NaOH). The process is best shown by a diagram:

$$\begin{array}{rcl} & 2\mathrm{Na} & \mathrm{Cl} \rightarrow \mathrm{Cl}_2 \uparrow \text{ (pos. wire)} \\ \text{(neg. wire) } \uparrow \mathrm{H}_2 \leftarrow 2\mathrm{H} & \mathrm{OH} & \end{array}$$

The chlorine Cl_2 and hydrogen H_2, being liberated, leave behind in the solution the constituents of 2NaOH:

$$2NaCl + 2H_2O + \text{Elect.} \rightarrow H_2 + Cl_2 + 2NaOH.$$

163. Preparation from Oxygen and Hydrogen Chloride. When hydrogen chloride and oxygen gases are heated, they interact very slowly to give water and chlorine. The action is greatly hastened by contact with cupric chloride. Lumps of pumice, saturated with a solution of this catalyst, or contact agent, are placed in a tube. When the mixture of gases is passed over the heated pumice (Fig. 37), steam, chlorine, and about 20 per cent of unchanged oxygen and hydrogen chloride issue at the other end:

Fig. 37

Skeleton equation: $HCl + O_2 \rightleftarrows H_2O + Cl_2.$
Balanced equation: $4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2$ (80%).

Longer heating does not alter the proportion of the materials successfully transformed. This is **Deacon's process.**

That 80 per cent is changed, and 20 per cent unchanged, is due to the fact that the action is *reversible.* If we lead pure chlorine and steam through the tube (read the equation backwards), 20 per cent of hydrogen chloride and oxygen are formed. No more than 20 per cent is formed, because these products are continually being used up again and reproduce steam and chlorine. If one product could be separated (p. 57) from the other, to prevent the backward action, the yield could be raised to 100 per cent. But all the four substances are gases (in the hot tube), and mix perfectly.

The result is interesting, because it shows that, under these conditions, oxygen is more active than chlorine in combining with hydrogen. We can try the experiment by mixing hydrogen with quantities of oxygen and of chlorine, *each* sufficient to combine with all the hydrogen. When we explode the whole mixture, we find that 80 per cent of the oxygen succeeds in uniting with hydrogen, but only 20 per cent of the chlorine is so used.

164. Preparation from Hydrochloric Acid and an Oxidizing Agent. The best way to make a supply of chlorine *in the laboratory* is to place potassium permanganate crystals ($KMnO_4$) in a flask (Fig. 38) and allow concentrated hydrochloric acid, previously mixed with an equal volume of water, to fall upon them drop by drop. The gas is rather soluble in water, and is best collected by displacing the air from bottles. When one bottle is full, it is stoppered and a fresh one substituted. To avoid the escape of the very irritating gas into the room, the tube from the collecting bottle dips beneath sodium hydroxide solution:

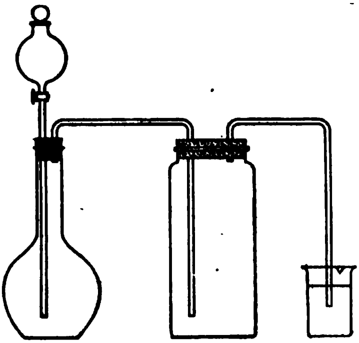

Fig. 38

$$2KMnO_4 + 16HCl \rightarrow 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2.$$

The essential feature of the chemical change is that the oxygen of the potassium permanganate unites with the hydrogen of the hydrochloric acid to give water. The potassium and manganese take as much chlorine as they require to form their chlorides, KCl and $MnCl_2$. The rest of the chlorine is liberated.

$KClO_3 + 6HCl \rightarrow KCl + 3H_2O + 3Cl_2$

This action is considered to be an *oxidation of the hydrogen chloride* by the permanganate, although the latter only removes the hydrogen, and does not reach the stage of adding any oxygen to the chlorine. The potassium permanganate, which carried the oxygen, is called the *oxidizing agent.* Since the permanganate *lost* oxygen, it was itself *reduced.* In all oxidations one substance is oxidized and another reduced.

Deacon's process (p. 107) is also an oxidation of hydrogen chloride (by free oxygen). The oxygen is reduced to water.

Chlorine may be prepared by using other substances to oxidize hydrochloric acid. Amongst those which are suitable are manganese dioxide MnO_2, potassium chlorate $KClO_3$ and red lead Pb_3O_4.

165. Physical Properties. Chlorine is a *greenish-yellow* gas, and takes its name from the Greek for this color. It has an exceedingly disagreeable *odor* and irritates the lining of the nose and throat. Alcohol vapor, or ammonia diluted with air, when breathed, relieve the irritation.

The *density* of the gas is recorded in the formula Cl_2. The 22.4-liter cube-full weighs 70.92 g., against 28.95 g. for air, so that chlorine is about 2½ times heavier. Two volumes of the gas *dissolve* in one volume of water at 20°. The solution is called **chlorine-water.**

The gas is *liquefied* by pressure below 146° (its critical temperature), the pressure required at 20° being 6.6 atmospheres. The liquid boils at −33°, and solidifies at −102° (its melting-point).

166. Chemical Properties. Chlorine is an element with about the same degree of activity as oxygen, and it unites with very much the same list of other elements. The compounds are called *chlorides.*

167. Unites with Metals. When powdered antimony (cold) and iron powder (warmed) are thrown into chlorine, they combine, and red hot particles of the chlorides, $SbCl_3$ and $FeCl_3$, fall to the bottom. Copper leaf (Dutch metal, used in "gilding"), or heated copper foil, burns in the gas, giving a fog of solid cupric chloride $CuCl_2$.

Skeleton: $Sb + Cl_2 \rightarrow SbCl_3$.
Balanced: $2Sb + 3Cl_2 \rightarrow 2SbCl_3$.

Sodium burns brilliantly in chlorine, giving sodium chloride. That a shining metal and a poisonous irritant like chlorine, in uniting, should yield a mild, household article like common salt illustrates very well the extraordinary nature of chemical change.

When thoroughly freed from moisture, chlorine no longer combines with metals like copper and iron. *Water* seems to be needed as a *contact agent,* in these, as well as in hundreds of other chemical actions. Hence, carefully dried chlorine, in liquid form, can be, and is stored and sold in iron cylinders (see detinning, § 638).

168. Unites with Hydrogen. A jet of burning hydrogen, lowered into a bottle of chlorine, continues to burn, giving hydrogen chloride HCl, the presence of which is shown by the fog produced by allowing the gas to come in contact with moist air:

$$H_2 + Cl_2 \rightarrow 2HCl.$$

Hydrogen and chlorine, mixed, do not combine when cold, provided strong light is excluded. But sunlight, or light from burning magnesium ("flashlight powder"), starts the combination, which occurs with explosive violence. Plunging a lighted taper into the mixture has, of course, the same effect.

169. Acts upon Compounds Containing Hydrogen. Because of its activity toward hydrogen, chlorine removes hydrogen from many compounds. Thus, if a lighted wax taper be plunged into chlorine, it continues to burn, though with a feebler flame. Dense smoke, composed of particles of free carbon, rise from the flame. Blowing the breath into the jar, afterwards, gives the fog due to hydrogen chloride. Thus the presence of hydrogen and carbon in the wax of the taper is proved. From this we learn, also, that chlorine has a relatively small tendency to combine with carbon. A few drops of warm *turpentine* ($C_{10}H_{16}$) upon a slip of filter paper will blaze up in chlorine, giving hydrogen chloride and an immense cloud of soot:

Skeleton: $C_{10}H_{16} + Cl_2 \rightarrow C + HCl.$
Balanced: $C_{10}H_{16} + 8Cl_2 \rightarrow 10C + 16HCl.$

170. Acts upon Water. We have seen that chlorine acts on steam, reversing Deacon's reaction to the extent of 20 per cent. It *acts also upon cold water,* when dissolved in the latter, although in a similarly incomplete way. With half-saturated chlorine-water at 10°, about one-third of the chlorine is used. One of the products, **hypochlorous acid** HClO, is of especial interest, because it is an exceedingly active substance, much used as an oxidizing agent (see §§ 375–6):

$$Cl_2 + H_2O \rightleftarrows HCl + HClO \ (33\%).$$

171. Unites with Non-metals. Phosphorus burns in the gas, giving the vapor of phosphorus trichloride PCl_3. Sulphur, when heated, combines more slowly, giving sulphur monochloride S_2Cl_2, used in vulcanizing rubber.

Although chlorine does not combine very readily with carbon, several compounds of carbon and chlorine are very important, such as chloroform $CHCl_3$ (§ 124) and carbon tetrachloride CCl_4 (§§ 124, 239).

172. Composition of Hydrogen Chloride. Now that we are familiar with the properties of chlorine, as well as with those of hydrogen, we may return to the question of the proportion by volume in which they are produced by decomposition of hydrogen chloride. When we electrolyze hydrochloric acid in the apparatus shown in Fig. 18 (p. 43), we find that the chlorine dissolves to a large extent in the liquid, and its true volume as gas is not easily ascertained. The apparatus (Brownlee's) in Fig. 39 avoids the difficulty by enabling us to saturate the liquid with chlorine before observing the collected gases. *The volumes of the two gases are* found to be *equal.*

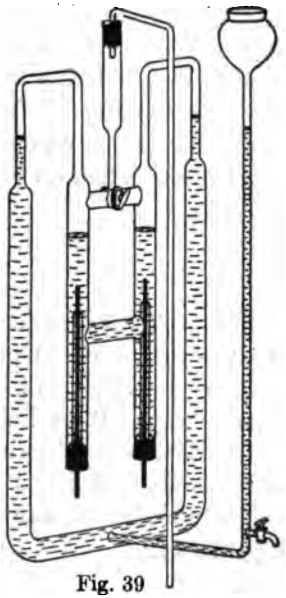

Fig. 39

A simpler apparatus (Fig. 40) may be used to show the same fact. The gases are generated, by electrolysis, in the test-tube, pass through the straight tube, driving the air before them, and finally bubble through sodium hydroxide solution. The whole apparatus must be covered with a dark cloth to exclude light, and handled in diffused light. In the course of fifteen minutes, the chlorine ceases to be dissolved, and the gases come off in their natural proportions. In half-an-hour

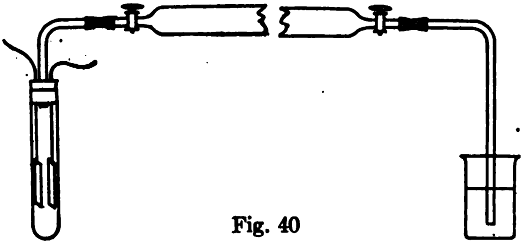

Fig. 40

English physician and chemist, 1643–1679

more they have filled the tube. The stop cocks are now closed, the tube is set in a tall cylinder containing potassium iodide (KI) solution (Fig. 41) and the lower stop cock is opened. The potassium iodide acts upon the chlorine, giving potassium chloride and free iodine, which is a solid,

$$2KI + Cl_2 \rightarrow 2KCl + I_2,$$

and the liquid rises until it *fills half the tube.* The remaining gas burns and is hydrogen.

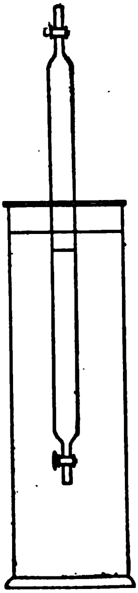

Fig. 41

The volume of the hydrogen chloride, in relation to the volumes of the constituents, may be learned by using a different apparatus (Fig. 42). A test-tube of heavy glass is filled with dry hydrogen chloride and closed with a rubber stopper greased with vaseline. A little sodium amalgam (solution of sodium in mercury) is introduced, and the stopper instantly replaced. When the contents are shaken for one or two minutes, the sodium combines with the chlorine and the hydrogen is liberated and remains. The mouth of the test-tube is then immersed in a jar of water, and the stopper withdrawn. The water rises and fills about *half* the tube.

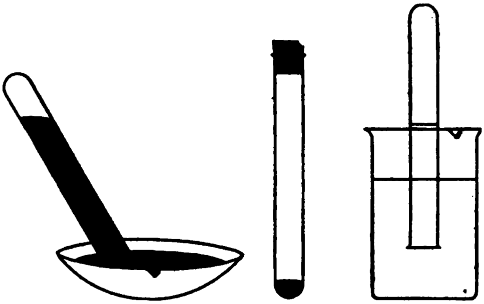

Fig. 42

Conclusion. The hydrogen has half the volume of the hydrogen chloride, and the volume of the chlorine is equal to that of the hydrogen. Therefore:

1 vol. hydrogen + 1 vol. chlorine → 2 vols. hydrogen chloride. This result further illustrates Gay-Lussac's law (pp. 49, 59).

173. Confirmation of the Formulæ Cl_2 and H_2. According to Avogadro's hypothesis, there are equal numbers of molecules in equal volumes of these gases. Let the rectangles represent small volumes, containing 1000 molecules each:

$$\overset{\text{Hyd. chloride.}}{\boxed{1000}\,\boxed{1000}} \quad \leftarrow \quad \overset{\text{Hyd.}}{\boxed{1000}} \quad + \quad \overset{\text{Chlor.}}{\boxed{1000}}$$

It appears from this that 2000 molecules of hydrogen chloride come from 1000 molecules of hydrogen and 1000 molecules of chlorine. Now, each molecule of hydrogen chloride contains hydrogen, so that the 1000 molecules of hydrogen must have given 2000 atoms of hydrogen, one for each molecule of the compound. Hence *each molecule of hydrogen contains two atoms.* The same is true of each molecule of chlorine. This confirms the conclusion we reached before (pp. 66, 82), namely, that the formulæ of the free gases are H_2 and Cl_2, and that single atoms of the elements occur only in combination (as in NaCl, HCl, etc.).

It would be more correct to reason that each molecule of hydrogen was split in two, and therefore contains *at least* two atoms. We find no need, however, of supposing that there are more than two atoms in each molecule.

Calculations.

174. Calculations Involving Volumes of Gases. For such calculations the simplest method is always to use the gram-molecular volume — the 22.4-liter cube.

175. Relative Densities of Gases. What are the relative weights of equal volumes of chlorine and hydrogen chloride? The formulæ record the weights of 22.4 liters: $Cl_2 = 2 \times 35.46 = 70.92$, and $HCl = 1.008 + 35.46 = 36.468$. The required relation is 70.92 : 36.468, so that chlorine is almost *twice* as heavy, bulk for bulk, as hydrogen chloride.

176. Density Compared with Air. We have seen (p. 71) that 22.4 liters of air weigh 28.95 g. Is water vapor heavier or lighter, at the same temperature and pressure? The formula, H_2O, shows that 22.4 liters of steam weigh $2 \times 1.008 + 16 = 18.016$. Air is heavier, in the ratio of 29 : 18, approximately.

177. The Volume of Gas from Given Weights of Material. What volume of oxygen is obtained by heating 15 g. of potassium chlorate? Follow the rules given (pp. 102–3) for calculating weights:

	$2KClO_3$	→	$2KCl$	+	$3O_2$.
Weights:	$2\,(39.1 + 35.46 + 3 \times 16)$		$2\,(39.1 + 35.46)$		3×32
or	245.12		149.12		96

Now, add the *volumes* in the case of substances which are *gases*. Here oxygen is the only one. Remembering that $O_2(=32$ g.) occupies 22.4 liters, the *volume* of the oxygen is 3×22.4 liters, or 67.2 liters. Then add the data given, and the x in their *proper places*. The x goes under the volume of oxygen:

$2KClO_3$	→	$2KCl$	+	$3O_2$.
245.12 g.		149.12 g.		96 g. or 67.2 liters
15 g.				x

The problem now reads thus: If 245.12 g. of potassium chlorate give 67.2 liters of oxygen, 15 g. of the former will give x liters of the latter:

$$245.12 : 67.2 :: 15 : x \ (= 4.07 \text{ l.}),$$

where x, the answer, is 4.07 liters of oxygen.

Observe that, when we use the gram-molecular volume, *one* proportion gives the answer. It is not necessary to make two steps in the calculation, by finding first the weight of the oxygen, and then its volume.

178. *Another Example.* What weight of copper will combine with 15.2 liters of chlorine (at 0° and 760 mm.)?

Cu	$+$	Cl_2	$\rightarrow$	$CuCl_2$.
63.57 g.		70.92 g. or 22.4 l.		134.49 g.
x		15.2 liters		

The proportion is:

$$22.4 : 63.57 :: 15.2 : x\ (= 43.14 \text{ g.}).$$

179. At Other than Standard Conditions. If the problem concerns a gas at some temperature and pressure *not* 0° and 760 mm., then correction must be made as a separate calculation. For example, if the 15.2 liters of chlorine, in the foregoing illustration, had been at 15° and 742 mm., then the volume would first have been reduced to 0° and 760 mm. It would serve the purpose equally well to correct the 22.4 liters to 15° and 742 mm.

180. Questions of Volume Alone. When weights are not mentioned in the question, but volumes only, the calculation is very simple. For example: What are the relative volumes of oxygen and hydrogen chloride used in Deacon's process?

	$4HCl$	$+$	O_2	$\rightarrow$	$2H_2O$	$+$	$2Cl_2$
Volumes:	4×22.4		1×22.4		2×22.4		2×22.4
Molecules:	4		1		2		2

Remembering that equal numbers of molecules occupy equal volumes, and that $4HCl$ = 4 molecules, O_2 = 1 molecule, etc., we perceive that 4 volumes of HCl will be required for 1 volume of oxygen.

Does the volume change during the process? Yes, $4 + 1$ volumes become $2 + 2$, or 5 volumes give 4.

If we measure the substances at a low temperature before and after the action, so that the steam condenses to water, then the volume shrinks to practically 2 volumes *of gas* (the chlorine). A gram-molecular volume of steam gives only 18 g. (or 18 c.c.) of water.

181. Warnings. The commonest mistake made in these calculations is to neglect to use, in the equations, the molecular formulæ. We must use H_2, O_2, C_2H_2 (acetylene), etc., (and not H, O, or CH), because the 22.4 liters hold the weights represented by the molecular formulæ.

Before calculating the volume (gaseous) of a substance represented in an equation, consider whether it is a volatile substance. Only volumes of *gases* can be calculated by the rules given above.

182. Exercises.

1. What would be the results of electrolyzing aqueous solutions of: (a) potassium chloride; (b) cupric chloride (*cf.* pp. 42, 106)?]

2. How should you separate the chlorine and the steam produced by Deacon's process?

3. Make equations showing the interactions with hydrochloric acid (p. 109) of: (a) manganese dioxide; (b) potassium chlorate; (c) red lead. Note that the remark about permanganate (p. 108, last par.) applies here also. The metals form $MnCl_2$, KCl, and $PbCl_2$, respectively.

4. What would be the pressure in a cylinder of liquid chlorine at 20°?

5. Make equations for the union of chlorine with: (a) copper; (b) sodium; (c) iron; (d) phosphorus; (e) sulphur.

6. When plunged into chlorine, a jet of illuminating gas continues to burn. A stream of soot rises from the flame, however, and blowing the breath into the jar, afterwards, produces a fog. What do you infer as to the constituents of illuminating gas?

7. What information is conveyed by the fact that the formula of the chloride of sulphur is written S_2Cl_2, and not SCl?

8. Make the molecular equation for the action of sodium upon hydrogen chloride (p. 113). Why does not the mercury interact with the latter (*cf.* p. 42)?

9. What facts led us, in Chap. VIII, to the conclusion that the molecular weight of chlorine was 70.92 while its atomic weight was 35.46?

10. What are the relative densities (p. 114) of: (a) oxygen and chlorine; (b) hydrogen and hydrogen chloride; (c) hydrogen and air; (d) acetylene C_2H_2 and air?

11. What volume of hydrogen chloride at 0° and 760 mm. is obtained by the interaction of 65 g. of sodium chloride, and an excess of sulphuric acid (pp. 95, 115)?

12. What weight of zinc is required to make 100 liters of hydrogen, at 10° and 750 mm., by displacement from sulphuric acid (pp. 79, 115)?

13. What are the relative volumes of the factors and of the products in the interaction between: (a) turpentine vapor and chlorine: (b) oxygen and carbon disulphide vapor (giving SO_2 and CO_2)?

14. What are the relative volumes of the products in the decomposition of: (a) mercuric oxide; (b) chlorine monoxide Cl_2O (chlorine and oxygen are formed)?

15. What are the relative volumes of the volatile substances concerned in the action of water vapor on iron (p. 79)?

16. Using the relative volumes in which oxygen and hydrogen combine to form steam, prove that each molecule of free oxygen is composed of at least two atoms (*cf.* pp. 49, 114).

17. (a) Calculate the weight of chlorine dissolved by 100 c.c. of water at room temperature (§ 165). (b) In half-saturated chlorine-water, what is the concentration of hypochlorous acid (p. 111)?

CHAPTER XIII.

SODIUM AND SODIUM HYDROXIDE.

183. In our study of common salt we have taken up one of its constituents, namely, chlorine, and its commonest derivative hydrochloric acid. The latter is a good example of an acid. We now turn to the other constituent, sodium, and one of its familiar compounds, namely sodium hydroxide ($NaOH$). The latter is an example of a different kind of substances, called *bases*. Salt, hydrochloric acid, and sodium hydroxide are examples of the three largest and most important classes of substances known to inorganic chemistry.

184. Preparation of the Metal Sodium. Sodium cannot be made by displacement (like hydrogen), because it is close to the top of the activity list (p. 42) of the metals, and no more active, and at the same time easily obtained, metal is available to displace it. It was first prepared by Davy (1807) by electrolyzing melted sodium hydroxide, and is still manufactured in this way. The aqueous solution of a sodium compound, such as sodium chloride, cannot be used, because, as we have seen (§ 162), hydrogen from the water is liberated in place of the metal.

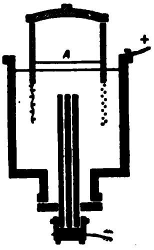

Fig. 43

The dry sodium hydroxide is melted (about 318°) in an iron vessel (Fig. 43), which is connected with the positive wire from the dynamo, and the oxygen is liberated on the iron (anode). The negative wire is connected with rods of carbon which stand up through the bottom of the vessel, and here (cathode) the sodium and the hydrogen are set free. Being lighter than the fused compound, the hydrogen rises in bubbles, and the sodium in melted globules, to the surface (*A*). Here they collect under an iron cylinder. The latter is made of wire-gauze at the lower part, to permit circulation of the liquid, but prevent the escape of the globules of sodium. It is closed at the top, to prevent the heated sodium from burning, as it would do if air could reach it. The melted sodium is ladled into cylindrical moulds, and the sticks of the metal are preserved in air-tight tin boxes.

185. Physical Properties of Sodium. Sodium is a *silver-like* metal, of specific gravity 0.97. It is *soft* and can be cut with a knife. It *melts* at 95.6° and *boils* at 742°. The gram-molecular volume of sodium vapor weighs 23 g., the same as the atomic weight, so that the molecular formula is Na.

186. Chemical Properties. Sodium burns in *chlorine*, giving sodium chloride NaCl. It burns also in *oxygen* (or air) to form sodium peroxide Na_2O_2. It acts violently on *water*, as we have seen (p. 38), displacing hydrogen and forming sodium hydroxide.

Skeleton: $Na + H_2O \rightarrow NaOH + H_2$.
Balanced: $2Na + 2H_2O \rightarrow 2NaOH + H_2$.

For this reason it tarnishes quickly in moist air. In the laboratory small amounts are kept under kerosene, which contains no compounds of oxygen.

As shown by its place in the activity list (Appendix V), the metal tends to form very stable compounds, and displaces the other metals (except potassium) from combination.

187. Uses. Sodium is used in the manufacture of many complex organic compounds. By contact action, it converts isoprene (C_5H_8) into caoutchouc $(C_5H_8)_x$ or raw rubber. This is a method of making rubber artificially, but it has not yet been used on a commercial scale. Sodium peroxide ("oxone"), made by burning sodium, is used as a source of oxygen (p. 25).

188. Preparation of Sodium Hydroxide. As we have seen, this compound is formed by the action of water on sodium, and may be obtained by evaporating the solution to dryness. But *manufacturing* it from an expensive substance like sodium is out of the question.

Much sodium hydroxide is made by boiling an aqueous solution of sodium carbonate Na_2CO_3 with slaked lime (calcium hydroxide, $Ca(OH)_2$):

$$Ca(OH)_2 + Na_2CO_3 \leftrightarrows 2NaOH + CaCO_3 \downarrow .$$

The calcium carbonate, which is chemically the same substance as lime-stone and chalk, is insoluble. All double decompositions are reversible, but here the precipitation of the calcium carbonate prevents it from acting upon the sodium hydroxide and reversing the action. After the precipitate has settled, the solution of sodium hydroxide is drawn off and evaporated to dryness.

189. Electrolytic Process. Sodium hydroxide is also manufactured by electrolysis of sodium chloride solution (pp. 106–7), the other product, chlorine, being of great commercial value also. In the Castner-Kellner apparatus (Fig. 44) the sodium chloride solution occupies the end compartments. The chlorine is liberated upon the carbon electrodes in these

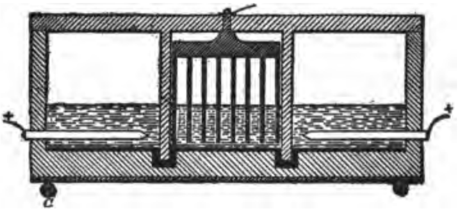

Fig. 44

compartments and rises to the surface. It is drawn off, dried, and compressed to liquid form in iron cylinders, or is made directly into bleaching compounds (§§ 375, 376). The sodium passes to the layer of mercury upon the floor of the box and dissolves in it. The box is caused to rock by the cam (*C*), so that the mercury (alone) flows under the partitions. In the center compartment the sodium leaves the mercury and proceeds towards the negative electrode which hangs here. The hydrogen of the water, being more easily liberated (as its place in the activity list shows), is set free and sodium hydroxide remains:

Skeleton: $Na + H_2O \rightarrow NaOH + H_2$.
Balanced: $2Na + 2H_2O \rightarrow 2NaOH + H_2$.

The solution is evaporated as usual. More salt can be added in the end compartments from time to time, so that the process is continuous.

190. Physical Properties of Sodium Hydroxide. The substance is a *white* crystalline solid. Generally it shows the form of the iron drums, into which it is run when melted, or of the sticks into which it is cast. It is exceedingly *soluble* in water. Its solution gives to objects the smooth, *soapy feeling* which is characteristic of alkalies. The solution is sometimes called **soda-lye,** and the solid, **caustic soda.**

191. Chemical Properties. Sodium hydroxide is exceedingly *stable,* being melted, but not decomposed, by heating.

The aqueous solution has an *acrid taste,* like soap or borax — a property common to all alkalies.

The solution acts upon *azolitmin* (contained in litmus extract or litmus paper), after it has been altered by a trace of acid into red litmus (p. 97), and changes the color *back to deep violet-blue.* This property is also shown by all alkalies.

Sodium hydroxide in solution *enters into double decomposition* with many substances, and, when one of the products is insoluble, the action is seen to be instantaneous. For example, with cupric chloride, it gives a precipitate of cupric hydroxide.

Skeleton: $NaOH + CuCl_2 \rightarrow Cu(OH)_2 \downarrow + NaCl.$
Balanced: $2NaOH + CuCl_2 \rightarrow Cu(OH)_2 \downarrow + 2NaCl.$

As this equation shows, sodium hydroxide behaves in such actions as if composed of (Na) and (OH). These actions, therefore, afford a ready means of making hydroxides of other metals. This property, again, is common to all alkalies.

Solutions of the alkalies also *act upon animal matter, e.g.* wool (p. 1), especially when hot, converting it largely into soluble substances. For this reason they are called *caustic* alkalies. They likewise act slowly upon the components of glass. For this reason a precipitate is often visible in the caustic soda reagent bottle, and the inner surface of the glass is always etched.

192. Alkalies and Bases. It will be seen that the chemical properties of sodium hydroxide may be summed up by saying that it is **an alkali.**

The alkalies, however, are simply the more soluble members of a much larger class of substances called **bases.** The less soluble bases, of which cupric hydroxide is an extreme example, do not show, distinctly, all the properties exhibited by alkalies. Thus, those which are least soluble have, naturally, no taste, do not visibly affect litmus, and are not soapy to the touch or corrosive towards glass. But they all show the tendency to double decomposition, in which the group (OH) is transferred, as it was from $NaOH$ to $Cu(OH)_2$ in the foregoing example.

193. Uses. Sodium hydroxide is used in immense quantities, along with fats, in the manufacture of soap. Some bleaching liquids are made by saturating its solution in water with chlorine. It is employed also in making many other sodium compounds which are used in the arts.

194. Exercises.

1. In the electrolysis of melted sodium hydroxide, why is the metal not liberated as a solid or as a vapor, but as a liquid?

2. Make molecular equations for the burning of sodium in chlorine and in oxygen.

3. Make equations showing the interactions of solutions of aluminium chloride $AlCl_3$ and of cupric sulphate $CuSO_4$ with sodium hydroxide (p. 123). Name the products.

CHAPTER XIV.

ACIDS, BASES, AND SALTS.

195. As we saw, at the opening of the preceding chapter, acids, bases, and substances with certain chemical properties similar to those of common salt form the vast majority of the compounds met with in inorganic chemistry. On account of their resemblance to common salt, the substances of the third class are called **salts.** We shall first recall the names and formulæ of some of the examples of these classes that we have already had occasion to mention.

196. Some Familiar Acids. The following are the acids we have mentioned:

Hydrochloric acid	HCl	Nitric acid	HNO_3
Sulphuric acid	H_2SO_4	Hypochlorous acid	$HClO$
Phosphoric acid	H_3PO_4	Acetic acid	HCO_2CH_3
Hydrofluoric acid	HF		

Acids are sometimes divided into **organic** acids, like acetic acid, **oxacids,** like sulphuric acid, and **hydracids,** like hydrochloric and hydrofluoric acids, which contain no oxygen.

197. Familiar Bases. The bases mentioned, with one or two additions (in italics), are:

Sodium hydroxide	$NaOH$	Calcium hydroxide	$Ca(OH)_2$
Potassium hydroxide	KOH	Cupric hydroxide	$Cu(OH)_2$
Ammonium hydroxide	NH_4OH	*Zinc hydroxide*	$Zn(OH)_2$

The name **alkalies** (p. 123) is applied to all the three *soluble* ones in the first column, and often to calcium hydroxide, although it is much less soluble.

198. Familiar Salts. Some of those already mentioned are:

Sodium chloride	$NaCl$	Potassium chlorate	$KClO_3$
Sodium sulphate	Na_2SO_4	Zinc sulphide	ZnS
Potassium nitrate	KNO_3	Sodium peroxide	Na_2O_2
Ammonium chloride	NH_4Cl	Sodium carbonate	Na_2CO_3
Cupric sulphate	$CuSO_4$	Lead sulphide	PbS
Cupric chloride	$CuCl_2$	Felspar	$KAlSi_3O_8$
Zinc chloride	$ZnCl_2$	Mica	(complex)
Zinc sulphate	$ZnSO_4$	Glass	(mixture)

199. Radicals. Upon comparing the formulæ in the lists, we notice that:

1. Every acid contains hydrogen, combined with one or more other atoms, constituting a group called **a radical.**

2. The very same radicals, such as SO_4, appear also in a *number of salts.*

3. Every base contains OH (the radical **hydroxyl**), and usually one atom, but occasionally more than one (as in NH_4) in the other radical.

4. The same radicals, combined in bases with OH, appear also in numerous salts.

5. Radicals may be simple, like H, Na, and Cl, or compound, like SO_4 and NH_4.

Since, in electrolysis, the hydrogen of an acid is attracted to, and is liberated at the negative electrode, it is called a **positive radical.** The rest of the molecule, as Cl or SO_4, is the **negative radical.** Similarly, every base contains OH as the negative radical, combined with a positive radical, as Na or NH_4. Again, every salt contains a positive radical, other than H, combined with a negative radical, other than OH. The name of each salt indicates the radicals of which it is composed.

As regards the salts in the second column, they show positive radicals, like K, Zn, and Na found in the list of bases. The negative radicals, ClO_3, S, O_2, and CO_3 are not in the list of acids we have met with. But there are well-known acids corresponding to them, namely, chloric acid $HClO_3$, hydrosulphuric acid H_2S, hydrogen peroxide H_2O_2, and carbonic acid H_2CO_3.

In general, then, all positive radicals combine with OH to give bases, all negative radicals combine with H to give acids. In general, also, each positive radical will combine with any negative radical to give a salt. In a few exceptional cases only, the compound can not be formed, presumably because it is unstable under ordinary conditions.

200. Reaction Formulæ. The formulæ of acids, bases, and salts are written in a uniform manner to show the behavior of the substances represented. Thus, the radical written first is usually the positive one which, in electrolysis, is attracted by the negative wire, and the negative radical follows. Again, in a compound like calcium hydroxide, the formula CaO_2H_2 would conceal the existence of the hydroxyl group. So the radicals are *written in brackets*, with the coefficient outside — $Ca(OH)_2$. Thus we write also $Cu(NO_3)_2$, and not CuN_2O_6, and $(NH_4)_2SO_4$, not $N_2H_8SO_4$. These formulæ are all reaction formulæ (p. 80). That is, they indicate, not simply the composition, but also the parts into which the compounds decompose, and from which they are formed in double decompositions (§ 146 and § 202, below).

201. Other Classes of Substances. The classification into the three groups, acids, bases, and salts, clears the ground wonderfully, for the substances we shall meet with, that are *not* included in one or other of these groups, are very few indeed. Of the substances *not* belonging to those classes, the following may be mentioned.

1. The **elementary substances**, of which there are about eighty. Of these we have mentioned a dozen.

2. The **oxides**, of which we have met some fifteen, including stannic oxide SnO_2, mercuric oxide HgO, and cupric oxide CuO. Theoretically, the oxides might be classed as salts, with the negative radical O. Water H_2O is the corresponding acid. But there are some objections to this view, and it is not at present adopted by chemists.

3. The **organic compounds**, of which carbon disulphide CS_2, formaldehyde CH_2O, alcohol C_2H_6O, turpentine $C_{10}H_{16}$, and others have been mentioned. There are many organic acids, bases, and salts. But the examples just named, as well as a vast number of other organic compounds, do not belong to any one of these three classes.

4. The **molecular compounds**, to which the hydrates, like $CuSO_4,5H_2O$ belong.

202. Properties Common to Acids, Bases, and Salts. There are *four* of these properties, three of which have come up repeatedly. These three form the subject of this section. (For the fourth property, see § 204.) All the four are chemical properties, that is, they involve some form of chemical change.

1. **Double Decomposition.** In solution, an acid or a base will interact with any salt. Acids also interact with bases and salts with salts. In all cases the action is a double decomposition (defined in § 146). For example:

Salt and acid: $AgNO_3 + HCl \rightarrow AgCl \downarrow + HNO_3.$
Salt and base: $Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + 2NaOH.$
Acid and base: $2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O.$
Salt and salt: $2AgNO_3 + CaCl_2 \rightarrow 2AgCl \downarrow + Ca(NO_3)_2.$

In each case a simple *exchange of radicals* occurs. When one product is *insoluble*, the action is instantaneous and complete.

In the third equation, where an acid and base interact, one of the products is necessarily water, obtained by the union of the H and OH. This case is called **neutralization,** for the special properties of the acid and base, such as the tastes and the actions upon litmus, disappear.

Many of these actions are used as *tests for the radicals* in unknown substances, because the appearances and colors of the precipitates differ more or less distinctly (p. 99).

These actions also furnish us with a general *method of making every substance of these three classes,* namely by choosing two other suitable substances containing the required radicals.

A radical is an atom, or group of atoms, which behaves as a unit in double decomposition.

2. **Displacement.** The *simple* radicals can be displaced, and the element liberated. Thus, we prepared hydrogen by adding metals to acids, and we absorbed chlorine by contact with potassium iodide solution (p. 113).

$$Zn + 2HCl \rightarrow H_2 + ZnCl_2.$$
$$2KI + Cl_2 \rightarrow 2KCl + I_2.$$

This does not apply to compound radicals.

3. **Electrolytes.** Solutions of acids, bases, and salts in water are *all* conductors of electricity. In *all* cases the solute is decomposed by the current. The separation is *always* into the two radicals, which are carried to opposite electrodes. Thus, all acids give hydrogen at the negative pole, the other radical passing to the positive pole.

Of all the properties they have in common, this one of being electrolytes is perhaps the most remarkable. It appears more surprising when we consider that *no* substances, other than acids, bases, and salts, undergo electrolysis in aqueous solution. This is an exclusive property of these classes of bodies.

It should be noted also that the water evidently has a good deal to do with the process. Alcoholic solutions behave in the same way. But solutions in benzene and carbon disulphide and many other solvents are non-conductors. The acids, bases, and salts, when pure and free from water, are also non-conductors.

203. The Conductivity of Electrolytes. The conducting power of solutions can be examined, roughly, by the apparatus in Fig. 45. The platinum electrodes are connected with a direct-current circuit. The lamp, which is on one of the wires, serves, by its resistance, to cut down the current. Its glowing also shows when the liquid is a conductor, and by varying brightness indicates roughly the conducting power of the solution.

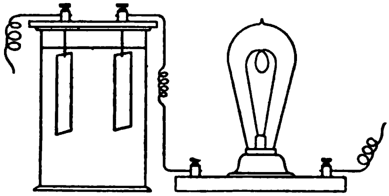
Fig. 45

A solution of sugar in water shows no conductance, and the lamp remains dark. Solutions of acids, bases, and salts in water enable the lamp to glow.

We quickly find that different substances, when they conduct, do so in different degrees. Hydrochloric and nitric acids conduct well. So do sodium and potassium hydroxides. Salts are practically *all* good conductors. But many acids, like acetic acid, conduct poorly. The same is true of some bases, like ammonium hydroxide.

Of course, "insoluble" substances give poorly conducting solutions. But in estimating the conductivity for chemical purposes, we take into consideration the amount dissolved. Thus silver chloride, being a salt, is an excellent conductor, when we allow for the extreme diluteness of the solution. The unit is the conducting power of one molecular weight of the substance, placed in solution between the electrodes.

204. Boiling- and Freezing-Points of Solutions of Acids, Bases, and Salts. We have seen (p. 91) that equal numbers of molecules dissolved in equal volumes of water raise the boiling-point to the same extent, and lower the freezing-point by a constant amount. Thus, one molecular weight of sugar (342 g.) or of glycerine (92 g.) dissolved in 1000 c.c. of water will raise the boiling-point from 100° to 100.52°, and will lower the freezing-point from 0° to −1.89°. But this is uniformly true only of substances which are *not* acids, bases, or salts. Molecular weights of substances of these three classes, in 1000 c.c. of water, raise the boiling point *more* than 0.52 degrees and lower the freezing point by *more* than 1.89 degrees. We say they give *abnormal* elevations of the boiling point and *abnormal* lowerings of the freezing-point.

Thus, a solution of 58.46 g. of sodium chloride in 1000 c.c. of water, boils at 100.94°, and freezes at −3.42°. The elevation in the boiling-point of the water is 0.94 degrees instead of 0.52 degrees. The effect is nearly *twice* as great as the normal one. The only conclusion we can draw is that nearly twice the usual number of molecules is present. In other words, **most of the molecules of the sodium chloride (but not all) have been broken into two parts by the water.** These sub-molecules are called **ions.** The decomposition into ions is a chemical change. It is the fourth **property** (§ 202) of acids, bases, and salts.

Further, we find that the abnormal effect *varies in amount*, yet not in an erratic manner, as the two following facts show:

205. Ions and Conductivity. The electrolytes which are *the best conductors* of electricity, such as hydrochloric acid, sodium hydroxide, and salts, *produce the greatest abnormal effects* upon the boiling- and freezing-points. On the other hand, *poor conductors*, like solutions of acetic acid and ammonium hydroxide, *give almost normal* elevations and depressions. Careful measurements show a close agreement in respect to conductivity, on the one hand, and elevation or depression on the other, throughout the whole list of hundreds of substances. This cannot be a chance coincidence, and demands explanation. It shows that **conductivity depends upon the parts of molecules we have called ions, and is proportional to their number.**

206. Ions and Radicals. The other fact is that, while substances like sodium chloride (NaCl) and nitric acid (HNO_3), *which contain only two radicals*, give effects approaching double the normal ones, *they never give more than twice the normal effect.* But substances like sodium sulphate Na_2SO_4 and calcium nitrate $Ca(NO_3)_2$, which contain *three* radicals, give effects approaching *three times the normal,* but not more. And substances containing *four* radicals, like ferric chloride $FeCl_3$, give effects approaching *four times the normal.* Evidently, solution in water tends to separate *all* the radicals from one another, and to break each molecule into as many separate particles as there are radicals in the substance. This indicates that **the radicals separate to form the ions.**

Apparently, therefore, the true basis of the four properties which are common to acids, bases, and salts is that *all substances of these three classes separate into ions when dissolved in water.* Hence, to save repeating the three words, we may name these substances, collectively, **ionogens** (Greek, *ion-producers*). The decomposition into ions is called **ionization.**

207. Ionization a Reversible Action. The depression in the freezing-point produced by sodium chloride was 3.42 degrees, instead of 1.89 degrees (§ 204, second par.). A depression of double the normal value would have been $2 \times 1.89 = 3.78°$. The decomposition was therefore incomplete. A decomposition of 81 per cent of the molecules would give the observed depression of 3.42°. We find, however, that the addition of more water increases the percentage of ionized material.

This is shown by measuring boiling-points, freezing-points, or conductivities. On the other hand, removal of water, by evaporation, causes some of the ions to unite. Finally, when all the water is gone, the solid that remains is, of course, composed wholly of molecules. **Ionization is therefore a reversible chemical action.**

$$\mathrm{NaCl} \rightleftarrows (\mathrm{Na}) + (\mathrm{Cl}).$$

208. Ions Bear Electrical Charges. We have yet to explain two facts, namely (1) how it is that ionogens in aqueous solution are decomposed by the current in electrolysis, and (2) how they have a power of conducting electricity proportional to the extent of their ionization (§ 205). The explanation, first offered by the Swedish chemist Arrhenius (1887), is startling, but satisfactory. It is, simply, that **the ions bear electrical charges.** In this respect they differ from ordinary molecules or atoms.

The constituents of the acid, base, or salt are liberated because the negative electricity on the negative electrode attracts all the positive ions in the solution, and repels all the negative ones.* At the same time, the negatively charged ions are attracted towards the positive electrode, and the positive ones repelled from it. The instant, therefore, that the circuit is completed, all the ions in the solution begin to move, or **migrate**, as it is called, towards their proper electrodes (Fig. 46). Ions (Greek, *going*) derive their name from this fact.

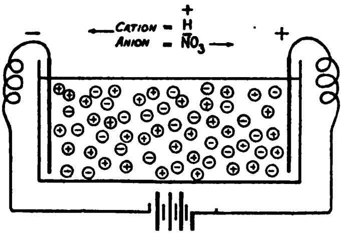

Fig. 46

The rest is easily understood. When a positive ion, say, of hydrogen, reaches and touches the negative electrode, its

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* In all circumstances, unlike charges of electricity attract one another, and like charges repel one another.

positive charge of electricity is neutralized, and the result is an ordinary atom of hydrogen. The atoms of free hydrogen unite to give molecules (H_2) and these form bubbles of the gas. If the positive ion is copper (the solution being one of cupric sulphate, let us say), then the copper atoms, when discharged, adhere to the electrode, and the latter becomes plated with copper.

Simultaneously with these operations, the negative ions are discharged at the positive electrode, and their material liberated.

As to the conductivity of the solution, we must remember that pure water does not conduct the current, except to an extraordinarily small extent. The conducting power of solution is due, therefore, to the ions. The more numerous the ions are, the greater will be the number of discharges taking place per second upon each electrode. So that the conducting power is naturally proportional to the number of ions, as we find it to be.

It must be noted that the electricity does *not* flow, as it does in a copper wire. In the wire the material is at rest, and the electricity *flows through* it. In the electrolyte *the particles of the substance themselves move,* and carry electricity with them.

209. Ionic Equations. Ionization is a kind of decomposition or rather dissociation, and is in every sense a chemical change. It is therefore expressed by equations. In these the *charges* upon the ions *must be shown,* as they are essential parts of the ionic substances.

$$NaCl \rightleftarrows Na^{+} + Cl^{-} \qquad FeCl_3 \rightleftarrows Fe^{+++} + 3Cl^{-}$$
$$Ca(NO_3)_2 \rightleftarrows Ca^{++} + 2NO_3^{-} \qquad Na_2SO_4 \rightleftarrows 2Na^{+} + SO_4^{=}$$

The number of positive charges must equal the number of negative charges. This is proved by several facts, and most simply by the fact that the solution of a substance like ferric chloride ($FeCl_3$) is electrically neutral, as a whole. Thus some ions carry one charge, like Na^+ and Cl^- and H^+, others two charges, like Ca^{++} and $SO_4^{=}$, and so forth. **An ion is an atom, or group of atoms, carrying an electric charge.**

The positive ions are called the **cations,** since they move toward the cathode. The negative ions are the **anions,** and move toward the anode.

We can usually tell which is the positive radical in a formula because it generally consists of one atom of a metallic element (K^+, Cu^{++}, etc.) or of hydrogen. The negative radical *may* contain a metal, like the Mn in $K(MnO_4)$, but always along with a non-metal like oxygen.

210. Possible Misunderstandings. Metallic sodium acts violently upon water. But the theory of ionization assumes that sodium atoms, in the form of ions (Na^+), can exist in water. The heavy electrical charge makes sodium-ion an entirely different substance from sodium.

When an ionogen is dissolved in water, a *part* dissolves to give *molecules*, and only a part gives ions. The solution of an ionogen is a *mixture* of water with *three* other (one molecular and two ionic) substances. The ions are the most active materials in the mixture.

It may be asked why ions with opposite charges do not unite. The answer is that they do unite. But other molecules dissociate, so that the *average* number of ions and molecules remains the same.

The charges are *not* derived from an electric current. They are upon the ions, as soon as the latter are formed, and are present at all times in all solutions of ionogens. The ions are formed by dissociation of the molecules, as quickly as the latter dissolve.

211. Ions and Double Decomposition. What we have just learned leads us to realize that there is, behind ordinary double decomposition, a more complex machinery than we had imagined. The ions are the active substances. Thus, in making sodium hydroxide, the equation

$$Ca(OH)_2 + Na_2CO_3 \rightarrow 2NaOH + CaCO_3 \downarrow$$

has to be modified to show the ions:

$$Ca^{++} + 2OH^- + 2Na^+ + CO_3^= \rightarrow 2Na^+ + 2OH^- + CaCO_3 \downarrow$$

When such solutions are mixed, the ions with opposite charges attract one another, so that some molecules of $CaCO_3$ are formed. This substance being insoluble, the molecules come out of solution, and more are formed, until the ions Ca^{++} and $CO_3^=$ are practically all used up. This is the mechanism when precipitation occurs.

When the mixture is filtered, and the filtrate is evaporated, the Na^+ and OH^- unite in increasing numbers, and finally the solid NaOH is obtained.

In *neutralization* (p. 129), an acid and a base give water and a salt:

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow H_2O + Na^+ + Cl^-$$

The H^+ and OH^- unite because, as we have seen, water is practically a non-conductor, and its *ions can not exist together*, save in a very small numbers. Thus a double decomposition may go to completion (without any precipitation) if the two interacting substances provide the ions of a substance which is very little ionized. The essential part of *all* neutralizations is contained in the equation:

$$H^+ + OH^- \rightarrow H_2O.$$

During subsequent evaporation, the ions of the salt (here Na^+ and Cl^-) unite, until all the water, including that produced by the action, is gone and crystals of the salt remain.

212. Ions and Displacement. When a metal acts upon a dilute acid, and hydrogen is liberated, the ions are again concerned in the mechanism of the action:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2 \uparrow$$
$$Zn + 2H^+ + 2Cl^- \rightarrow Zn^{++} + 2Cl^- + H_2 \uparrow$$

From this it appears that each zinc atom simply takes the positive charges from two hydrogen ions of the acid. The discharged hydrogen then escapes. Thus all displacements are of the form:

$$Zn + 2H^+ \rightarrow Zn^{++} + H_2.$$

213. Properties Peculiar to Acids. An acid has the four properties possessed by all ionogens, with the additional feature that one radical is always H. Thus:

1. With bases and salts it gives double decompositions, using H as one radical.
2. Its hydrogen radical is displaced by certain metals.
3. Its solutions are electrolytes and hydrogen is liberated at the cathode:

$$2H^+ + 2\ominus \rightarrow H_2.$$

4. It is ionized in aqueous solution.

If sufficiently soluble, it has, in addition, a sour taste and a special action on litmus (turning it red, a test first discovered by Boyle), both due to the hydrogen radical.

Many other substances, such as sugar $C_{12}H_{22}O_{11}$, contain hydrogen, but lack these properties, *and therefore do not contain hydrogen as a radical,* and are not acids.

Briefly, **an acid is a substance which contains hydrogen as a positive radical, and, if soluble, has the sour taste and the action on litmus of this radical.**

An **active** or **strong acid is one which is very largely ionized,** giving much hydrogen-ion (like HCl), and therefore shows the properties of the radical H very markedly. **A weak acid is one which is very little ionized,** like acetic acid.

214. Properties Peculiar to Bases. The base has the four properties of an ionogen, one of its radicals being **hydroxyl** OH:

1. In double decomposition with acids and salts it exchanges OH for another negative radical.

2. In electrolysis, the OH liberated, at the anode, gives water and oxygen

$$4OH^- + 4\oplus \rightarrow 2H_2O + O_2.$$

3. Its positive radical is displaced by other metals.

4. It is ionized in aqueous solution.

If sufficiently soluble, it shows, when dissolved, the soapy taste and feeling, and the special action on litmus (turning red to blue), both due to the OH radical.

Many other substances (such as sugar $C_{12}H_{22}O_{11}$) contain OH, but it is not the presence of these elements, but their presence *as a radical* that makes a substance a base.

Briefly, **a base is a substance which contains hydroxyl (OH) as a negative radical and, if soluble, has the taste and action on litmus of this radical.** Strong bases, like sodium hydroxide, and **weak** ones like ammonium hydroxide, differ in the same way that strong and weak acids differ. That is, weak bases are little ionized, and show the properties of a base less markedly.

215. Activity of Metals and Strength of Bases. It will be observed that the most active bases (alkalies) are hydroxides of the three metals (K, Na, Ca) which come first in the activity-list (p. 42). We may therefore judge the activity of a metallic element, at least roughly, either by trying its displacing power as a metal, or by measuring the activity (degree of ionization) of its hydroxide.

216. Salts. As we have seen, **salts are substances containing a positive and a negative radical, other than hydrogen and hydroxyl.**

Some salts do indeed contain (H) or (OH) as a radical, but always *in addition to* two other radicals. Thus we obtained sodium-hydrogen sulphate, $NaHSO_4$, which gives H^+, as well as Na^+ and $SO_4^=$. This is an **acid salt.** Basic calcium chloride $Ca(OH)Cl$ is a **basic salt.**

217. Exercises.

1. By what experiments should you determine which were the radicals in substances of the following composition: $Cu(NO_3)_2$, $C\,CaO_3$, $NBrH_4$, H_4IN, ClO_4K, $MnHO_4$. There are always two ways, and usually three, of determining the radicals — what are they (§ 202)?

2. How should you determine whether a given substance were an acid, base, or salt (*i.e.* an ionogen), or not?

3. When do the ions receive their charges of electricity?

4. Using the models given in § 209, make the ionic equations representing the ionization of all the acids, bases, and salts, the formulæ of which are given in §§ 196, 197, 198.

5. Which are the anions and which the cations in the substances whose formulæ are given on p. 128?

6. Using the models in §§ 213 and 214, make equations for the liberation of copper and of chlorine by electrolysis.

7. Make an ionic equation (§ 212) for the displacement: (a) of hydrogen from dilute hydrochloric acid by magnesium; and (b) of copper from cupric sulphate solution by zinc.

CHAPTER XV.

VALENCE.

The differing number of charges on different ions has called our attention vaguely to a subject which must now be explored and set forth more clearly.

218. Valence. The formulæ of a number of common compounds, including some that we have met with, are as follows:

$$\begin{array}{llll} NaCl & ZnCl_2 & SbCl_3 & SnCl_4 \\ NaBr & ZnBr_2 & SbBr_3 & SnBr_4 \\ NaI & ZnI_2 & SbI_3 & \end{array}$$

We observe that one atomic weight of sodium appears to unite with only one unit of another element, one unit weight of zinc with only two units of another element, a unit of antimony with not more than three, and a unit of tin with only four units.

It seems that *an atomic weight of each element has a fixed capacity for combining with not more than a certain number of atomic weights of other elements.*

Other compounds of only two elements have the formulæ:

$$HCl \quad H_2O \quad NH_3 \quad CH_4 \quad Li_3N \quad CCl_4.$$

Apparently Cl combines with only one atom of another element, O with two atoms, N with three atoms, C with four atoms. Also an atom of hydrogen combines with not more than one atom of another element, although it may take more than one atom of hydrogen to satisfy the atom of that other element (H_2O, CH_4, etc.).

This limited combining capacity of each kind of atomic weight (or atom) is called its **valence.**

219. Marking the Valence. Until we are familiar with their values in each case, it may be well to mark the valences thus:

$$Na^{I}\quad Zn^{II}\quad Sb^{III}\quad Sn^{IV}\quad Cl^{I}\quad Br^{I}\quad I^{I}\quad O^{II}\quad N^{III}\quad C^{IV}$$

As we should expect, an atom with the double capacity can combine with two of the single capacity, *or with one of the double capacity,* and so forth. Thus we have compounds of oxygen:

$$Zn^{II}O^{II}\quad Sn^{IV}O_2{}^{II}\quad Sb_2{}^{III}O_3{}^{II}\quad N_2{}^{III}O_3{}^{II}$$

Briefly stated, the quantities of the two elements which combine must have equal total combining capacities. Thus Sn^{IV} has the capacity four, and $O_2{}^{II}$ has the total capacity of 2×2 or 4: $Sb_2{}^{III}$ has a total capacity of 2×3 (or 6) and so has $O_3{}^{II}$ $(3 \times 2 = 6)$.

The unit of combining capacity of an atomic weight (or atom) is called a valence. The atomic weights of H and Cl are said to be **univalent**; those of Zn and O, **bivalent**; those of Sb and N, **trivalent**; those of Sn and C, **quadrivalent.** The highest valence known is eight.

220. Valence and Ionic Charges. Comparison with the formulæ of the ions already given will now show that the valence is equal to the number of charges on the corresponding ions: $H^{I}Cl^{I}$ gives $H^+ + Cl^-$ and $Zn^{II}Cl_2{}^{I}$ gives $Zn^{++} + 2Cl^-$. Also, of course, the total number of each kind of charges (positive and negative) was equal, just as the total valences of each of two constituents of each compound are equal. We shall return, later, to the supposed cause of this correspondence between valence and the numbers of charges.

221. Valence of Radicals. What has been said applies to compounds of not more than two elements — so called, **binary compounds.** We cannot, by inspection, tell the valences in a compound of three or more elements, like H_2SO_4. But, as we have seen, all ionogens *behave like* binary compounds, because they divide into radicals, which move *as wholes* from one state of combination to another. Hence we can assign a valence to the radical SO_4 *as a whole.* It is evidently bivalent, $H_2^{I}(SO_4)^{II}$, $Zn^{II}(SO_4)^{II}$. Also, in $K^{I}(NO_3)^{I}$, and in $H^{I}(NO_3)^{I}$, the NO_3 is clearly univalent. $H_3^{I}(PO_4)^{III}$ shows PO_4 to be trivalent.

222. Valence also by Displacement. In the foregoing instances, we have learned the valence of an element or radical by studying its combinations. But, clearly, if an element is displaced from combination, atoms of equal total valence must take its place. Thus the action:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

shows Zn displacing $2H^{I}$, and the valence of Zn must therefore be two. We see that this is the case for, on displacing the 2H, the Zn *combines with* $2Cl^{I}$.

223. Summary. We may now sum up all these facts by saying: The **valence of an element is a number representing the capacity of its atomic weight to combine with, or displace, atomic weights of other elements, the unit of such capacity being that of one atomic weight of hydrogen or chlorine.** To make a corresponding statement for the valence of a radical, we substitute, in the foregoing sentence, the word *radical* for element, and the word *formula-weight* for atomic weight.

224. Application in Making Formulæ and Equations. We can see at once that the rule of valence will be of great assistance to us in making formulæ and equations. Suppose, for example, that we burn a piece of aluminium foil in chlorine and get the white aluminium chloride. What is its formula? Up to this point, we should simply have looked for it in a book. And if, subsequently, we had required the formulæ of the oxide and sulphate of aluminium, we should have looked these up *separately* also.

But now, all we have to do is to *find out the valence of aluminium.* Knowing already the valences of Cl^{I} and O^{II} and $(SO_4)^{II}$, we have then all the information we require for making the needed formulæ. Suppose we know that the atomic weight of aluminium is trivalent Al^{III} (see next section, § 225). Making the total valences of each half of the compound alike, we get the formulæ:

$$Al^{III}Cl_3{}^{I}, \quad Al_2{}^{III}O_3{}^{II}, \quad Al_2{}^{III}(SO_4)_3{}^{II}.$$

When we know the valences of the elements and radicals, we can make the formula of any required compound.

The reader must therefore make a special effort always to learn the valences of each element and radical, and always to use them in making formulæ.

The reader must also always *check every formula he writes from memory,* to make sure that it is correct. Thus, if he thinks the formula of zinc nitrate is $ZnNO_3$, he must count the valences, $Zn^{II}(NO_3)^{I}$. Evidently, the *correct* formula is $Zn(NO_3)_2$.

225. How to Find out a Valence. To find out the valence of an element, the first time we meet with one of its compounds, take the formula of one simple compound of the element, containing an element of known valence. Thus, what is the valence of thorium? The oxide of this metal forms 99 per cent of the mantel of an ordinary incandescent gas-burner. By referring to any book on chemistry, we find that the formula of this oxide is ThO_2. The total valence of the oxygen is $O_2{}^{II}$ or 4. The valence of Th must therefore be four, Th^{IV}.

What is the valence of phosphorus in the pentoxide, P_2O_5? $P_2{}^{x}O_5{}^{II}$. $2 \times x = 5 \times 2$. Hence $x = 5$, and the valence of P is five, P^{V}.

It is clear, also, that *to be able to recall the valence of each element,* we must memorize the formula of at least *one* simple compound of each element.

226. Elements with More than One Valence. The rule of valence is not so simple as it has thus far appeared to be. A number of the elements have more than one valence. In other words, the capacity of an atomic weight of such an element may have two (or even more) values, according to the circumstances under which it is combining with other elements.

Thus, antimony is usually trivalent, and gives compounds like $SbCl_3$, Sb_2O_3, $SbBr_3$. But it can also form compounds in which it is quinquivalent, like $SbCl_5$. Similarly, iron forms two complete series of compounds:

Bivalent: $FeCl_2$, FeO, $Fe(OH)_2$, $FeSO_4$.
Trivalent: $FeCl_3$, Fe_2O_3, $Fe(OH)_3$, $Fe_2(SO_4)_3$.

When an element does give more than one series of compounds, however, we always make a strong point of this fact, so that it may not be overlooked.

No simple rule, for telling, in advance, which valence will be used in a given action, can be stated. But the ions Fe^{++} and Fe^{+++}, for example, have different properties, and are easily recognized in practice.

227. Exceptional Compounds. A few compounds will be met with in which an element shows an exceptional valence. Thus, nitrogen gives two series of compounds of N^{III} and N^{V}. But there are three oxides, N_2O, NO, and NO_2, in which the valence of nitrogen seems to be one, two, and four, respectively. However, these are single compounds, not belonging to any series, and are the only compounds of nitrogen showing any of those three valences. Those valences are exceptional.

Again, FeO and Fe_2O_3 belong to the two regular series of compounds of iron. But there is the magnetic oxide, Fe_3O_4, where the valence of iron appears not to be a whole number, but 8/3 or $2\frac{2}{3}$. In this case the chemist makes the valence regular by supposing the magnetic oxide to be a compound of the other two oxides, and writing its formula, FeO,Fe_2O_3.

228. A List of Valences and Charges. The following table contains the valences of some familiar ions and the *commonest* valences of some elements. Many of these elements, however, possess other regular valences, in addition to those shown, so that *the list does not pretend to be complete.*

Univalent.	Bivalent.	Trivalent.	Quadrivalent.
Na^+	Ca^{++}	Al^{+++}	Sn^{++++}(stannic)
K^+	Ba^{++}	Fe^{+++} (ferric)	SiO_4^{----}
H^+	Mg^{++}	Cr^{+++}	C (CH_4, CO_2)
$(NH_4)^+$	Zn^{++}	Sb^{+++}	
Ag^+	Pb^{++}	Bi^{+++}	
Cl^-	Ni^{++}	$(PO_4)^{---}$	**Quinquivalent.**
Br^-	Co^{++}	As (AsH_3)	
I^-	Mn^{++}	B (B_2O_3)	N (N_2O_5)
F^-	Cu^{++} (cupric)	N (NH_3, N_2O_3)	P (P_2O_5)
$(OH)^-$	Fe^{++} (ferrous)	P (PH_3)	As (As_2O_5)
$(NO_3)^-$	Hg^{++} (mercuric)		
$(ClO_3)^-$	Sn^{++} (stannous)		
	O^{--}		**Sexivalent.**
	$(SO_4)^{--}$		
	S^{--}		
	$(CO_3)^{--}$		S (SO_3)
	O_2^{--} (peroxide)		

Where no charges are indicated, the element, by itself, does not ordinarily form an ion.

229. The Cause of Valence. The number of charges on an ion is equal to its valence. We have recently gained some idea of the reason for this. Electricity is made up of small units of *negative* electricity, called **electrons.** The mass of an electron is about one thousandth of that of a hydrogen atom. A negative charge on an atom of an element means that an electron has been added to the atom. A positive charge means that an electron has been taken from a neutral atom, leaving it positive. Thus an ion of chlorine (Cl^-) is equivalent to an atom plus an electron ($Cl+\epsilon$), an ion of hydrogen, an atom minus an electron ($H-\epsilon$). When these two ions combine, a neutral molecule of HCl is formed.

Assuming this theory, valence is easily explained. It appears that an atom of chlorine can take up one electron, but not more than one, giving a stable structure. H can lose one electron, but not more. Zn, however, can lose two, giving Zn^{++}, and S can gain two, giving S^{--}, and Al can lose three Al^{+++}.

If Al^{+++}, lacking three electrons, combined with only $2Cl^-$, the combination would still have a unit positive charge and would tend to attract another electron (with its attached atom). In this view the atoms of two substances tend to combine in such numbers that the electrons carried by one kind of the atoms (the negative) just suffice to supply the electrons lacking in the other kind (the positive). Chemical combination is a sort of neutralizing operation, and valence is the measure of the excess or deficiency of electrons on each kind of atom or radical.

230. A Suggestion. Having just discussed the conception of valence, we have now considered all the laws of chemical composition. At this point the reader should pause and *review thoroughly the subjects of the first fifteen chapters.* The understanding of the fundamental principles which this retrospect will give will greatly lighten the task of understanding the new and more complex substances we shall have to consider, and the new kinds of reactions and new conceptions we shall encounter, in the chapters immediately following.

231. Exercises.

1. Mark the valences in the formulæ: $InCl_3$, V_2O_5, OsO_4, $PtCl_4$.

2. Mark the valences of the radicals in the formulæ: $Zn(SeO_4)$, $Al_2(TeO_4)_3$, $H_3(AsO_4)$, $H(SbO_3)$.

3. If 26 g. of chromium displace 1 g. of hydrogen from hydrochloric acid, what is the valence of chromium in this displacement (see Table of Atomic Weights)?

4. Correct the following formulæ: $ThNO_3$, $ThPO_4$, $Al(PO_4)_2$, NaO, PbF, $Bi(NO_3)_2$.

5. One gram of a quadrivalent element unites with 0.27 g. of oxygen. What is the atomic weight of the element?

CHAPTER XVI.

CARBON. THERMOCHEMISTRY.

232. We have now covered all the rules regarding the composition of compounds, and we have learned something of the common classes of chemical substances. We next become impatient to know the nature of the kinds of matter composing the bodies of animals and of plants, the materials used in cooking and cleaning, and the coal and illuminating gas we burn. Upon examining wood and coal, fat and starch, soap, sugar, and gasoline, we find that one element is common to all, namely carbon. The same element is found in limestone (calcium carbonate $CaCO_3$) and other rocks. In the present chapter we shall study the forms of the element itself. Its marvellous array of diverse compounds can then be taken up in later chapters.

THE FORMS OF CARBON.

233. Carbon is known in a variety of forms. Graphite, charcoal, and the diamond are all simply free carbon. We know this because each, when burned in air or oxygen, gives nothing but carbon dioxide gas:

$$C + O_2 \rightarrow CO_2.$$

234. Allotropic Forms. Many substances, like water, may exist in the three states of solid, liquid, and gas. But with most substances three is not the limit (p. 51). Several solid forms or states, in which the physical properties are as different as are those of diamond and charcoal, are shown by many substances. Such different forms are called **allotropes.** In the case of carbon the differences are familiar to everyone.

The diamond is transparent and crystalline, while charcoal is opaque and non-crystalline. The former is, bulk for bulk, three and one-half times as heavy as water, while the latter floats on water and, even when the air is removed from its pores, has a specific gravity less than 2. When burned, 1 g. of carbon gives out differing amounts of heat according to the form used. Thus diamond gives 7805 calories (p. 50), graphite 7850, and sugar charcoal 8040.

The various forms of carbon are all insoluble in ordinary solvents. Molten iron dissolves carbon, however.

235. Diamond. The diamond is distinguished by its natural crystalline form, which often resembles the octohedron (Fig. 30, p. 88). For ornamental purposes it is "cut" by grinding new faces so as to give artificial forms, called "brilliants" (Fig. 47) and "rosettes." It is the hardest of familiar substances, and can be scratched or polished only by rubbing with diamond powder. The colorless stones and those with special tints are valuable. The black ("carbonado") and badly colored specimens are less valuable and are used for grinding, for glass-cutting, and on the points of drills.

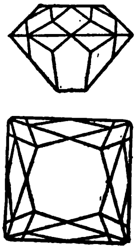

Fig. 47

Diamonds are found chiefly in South Africa and Brazil. They are separated from the rock by weathering and washing. They are sold by the carat (1 carat = 4 grains = 205 mgms.*) and the value increases with the size. Thus a first quality, cut stone of 1 carat is worth about $270, one of 2 carats about $340 per carat. The largest known specimen, the Cullinan, weighed 3032 carats before being cut.

236. Graphite is found in nature in Siberia, Cumberland, Brazil, Ceylon, and elsewhere. It forms dark grey or black

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* The new international carat (legal in U. S., 1913) weighs 200 mgms.

hexagonal tablets, and, when pulverized, it gives slippery scales of microscopic size. Unlike the diamond, it is quite soft, has a specific gravity of 2.3, and conducts electricity. Natural graphite is usually mixed with foreign matter, and even the purest specimen leaves, when burned, from 2 to 5 per cent of ash. It is called also **plumbago** and **black lead.**

Graphite (Greek, *I write*) is forced through dies to form the cores of "lead" pencils (first used in the 16th century). Clay is first added in varying proportions to give different degrees of hardness. Because of its conductivity for heat, it is used to make crucibles. Smeared on a plaster cast (non-conductor), it gives a conducting surface on which metals (copper or silver) can be deposited by electrolysis. A thin layer, used as stove-polish, protects the iron from rusting. In electro-chemical industries it is used for electrodes at which chlorine is to be liberated; all other conductors interact chemically with this element and are destroyed. It is employed also as a lubricant.

Large amounts of pure graphite are now manufactured by heating coke with some pitch and a little sand or ferric oxide (Acheson's process). The mixture (3 to 3½ tons) is piled (Fig. 48, p. 153) between the electrodes connected with a dynamo, and, on account of its high resistance, becomes strongly heated. The operation is complete in from 24 to 30 hours.

237. Amorphous Forms of Carbon. The non-crystalline or amorphous (Greek, *without form*) varieties of carbon are numerous. They include **wood-charcoal, lampblack, animal charcoal, coal** (*e.g.*, bituminous coal and anthracite) and **coke.** Of these lampblack (see § 277) contains the greatest amount of free carbon, and bituminous coal the least. The latter contains the largest proportion of compounds of carbon. Coke is made by heating coal (air excluded) until all the moisture and volatile matter (such as cause burning coal to give smoke) are driven out. Charcoal is made in the same way from wood. These two substances will be discussed after we have learned something of the chemistry of plants (§ 573), from which they are formed by decomposition.

238. Chemical Properties of Carbon. 1. Carbon *unites* vigorously *with oxygen.* With an excess of oxygen it forms carbon dioxide, a gas:

$$C + O_2 \rightarrow CO_2.$$

With a limited supply of oxygen, it forms carbon monoxide, also a gas:

$$2C + O_2 \rightarrow 2CO.$$

2. In consequence of this tendency to unite with oxygen, carbon is much used as a *reducing agent.* Thus, when oxide of copper is heated with pulverized charcoal, carbon dioxide is formed, and the metal is liberated:

$$2CuO + C \rightarrow 2Cu + CO_2.$$

In the same way the oxides of tin, of lead, and of many other metals may be reduced. Copper, tin, and lead are manufactured from the ores in this way.

3. Carbon *unites directly with some elements,* particularly with sulphur to form carbon disulphide CS_2 (§ 346) and with certain of the metals. Thus, when dissolved in molten iron, it forms **iron carbide** Fe_3C.

An interesting case is the union of carbon with *hydrogen.* The union is ordinarily too slow to be observed. But when the carbon is mixed with pulverized nickel (contact agent) and hydrogen is passed over the mixture at 250°, methane CH_4 is formed (99 per cent). At higher temperatures the union is less complete and, at 850°, reaches only 1.5 per cent. In the arc, however, direct union to form acetylene C_2H_2 takes place. Dozens of compounds containing only hydrogen and carbon, in different proportions, are known (Chap. XVIII), but all the others are obtained by indirect reactions.

The *valence* of carbon is almost always *four*. This is clearly seen in $C^{IV}O_2^{II}$ and $C^{IV}H_4^{I}$. In a very few compounds, of which CO is the commonest, carbon is bivalent.

239. Carbon Tetrachloride CCl_4. This compound is manufactured by leading dry chlorine into carbon disulphide, in which a little iodine (contact agent) is dissolved:

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2.$$

On distilling the resulting mixture, the carbon tetrachloride CCl_4 (b.-p. 77°) passes off and is condensed, while the sulphur monochloride S_2Cl_2 (b.-p. 136°) remains. The latter compound is purified by separate distillation, and is used in vulcanizing rubber. As now made, carbon tetrachloride costs, wholesale, only 10 cents per pound.

Carbon tetrachloride is a colorless liquid. It dissolves fats and tars and other organic compounds, and has the advantage over benzine and gasoline of being non-inflammable. It is therefore used in taking the grease out of wool, linen cloth, oil-bearing seeds, and bones. "Carbona," sold for removing stains from, and cleaning ("dry cleaning"), clothing, gloves, etc., is benzine (see § 266) to which sufficient carbon tetrachloride has been added to render the mixture non-inflammable. "Pyrene" fire extinguishers contain a liquid which is mainly carbon tetrachloride. When the liquid is directed upon burning material, the carbon tetrachloride is vaporized. The vaporization cools the mass by using up the heat (p. 50), and the vapor at the same time displaces the air and stops the combustion.

240. Carbides and the Electric Furnace. Chemical actions which proceed only at very high temperatures are most economically carried out by using electricity as the source of heat. In such cases the electricity has no electrolytic or other chemical action. There are two types of electric furnaces. In the making of graphite (p. 150) and of carbon disulphide (§ 346), which illustrates one of them, the resistance of the carbon furnishes the occasion for the rise in temperature.

Of the same type is the furnace used for making **carborundum** (SiC, carbide of silicon), of which hundreds of tons are manufactured annually at Niagara Falls (Acheson's process). The coke and sand (silicon dioxide SiO_2) are piled between the terminals, and the resistance of the former causes the production of the heat (Fig. 48):

$$3C + SiO_2 \rightarrow SiC + 2CO \uparrow .$$

Here the carbon reduces the oxide, and combines with the element (Si) as well. The product (SiC) is exceedingly hard, and, after pulverization and mixing with other materials, is moulded into grinding wheels.

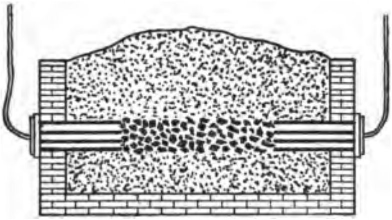

Fig. 48

In the other type of furnace the air between the terminals furnishes the resistance, and the *arc* (a discharge carried by the badly conducting air and carbon vapor) furnishes the heat.

The arc is used in making **calcium carbide** (CaC_2), by heating a mixture of lime (CaO) and coke:

$$CaO + 3C \rightarrow CO + CaC_2.$$

Cold water acts vigorously with calcium carbide, giving **acetylene** gas C_2H_2 (see § 268) and calcium hydroxide (slaked lime):

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \uparrow$$

THERMOCHEMISTRY.

241. Heat and Chemical Change. We decompose potassium chlorate because we desire to get oxygen. We burn phosphorus when we require some phosphorus pentoxide. Chemical changes are used for the purpose of making hundreds of needful materials. But chemical changes, in many cases, produce *heat*, as well as new materials, and it is quite as often the heat, and not the new substance, that we want for commercial purposes. We sometimes use *both*, but more often one is thrown away.

In the steam engine we burn coal, not to obtain carbon dioxide, but heat — heat to generate steam and obtain motion and do work of some valuable description. In the gas or gasoline (petrol) engine we burn (explosively) a mixture of air and combustible vapor, and we use the force of the explosion to do work, while the material products of combustion pass into the atmosphere. The **heat** is therefore to be kept in mind as one of the real and most important products of many chemical changes.

242. Heat and Energy. Heat was formerly thought of as a kind of matter, which simply lacked weight. The heat of the engine is used up in turning the dynamo, and *electricity* is set in motion. The electrical energy can be turned into *light*, as in the arc lamp or into heat by passing through a thin wire, as in the tungsten bulb. Light can be *turned back* into heat by falling on a black body. None of these things have weight, and each can be turned into any of the others. In both of these ways they differ from matter, the forms of which cannot be changed one into another. To mark these differences a separate name is now used, and heat, light, and electricity are called forms of **energy.** **Energy is something that can do work.** It resembles matter only in the fact that it **can be kept, or changed from one form to another, without loss in its quantity** — a fact called the principle of the **conservation of energy.** Hence energy is bought and sold like matter.

243. Internal Energy. The heat in a tungsten lamp arises because electrical energy is being changed. The electricity in a wire comes from the motion and heat of the engine, which are being used up. Since energy cannot be created from nothing, we look for the source of every development of energy in a supply of some other variety. Hence, when heat is given out in a chemical change, we assume that there was energy in some other form in the original matter — such as the oxygen and carbon — and this form we call **chemical** or **internal energy.** It is this energy that gives their value to our coal-beds, our batteries, and our explosives, not the particular materials they may contain.

It is the internal energy of coal or coke and oxygen that we use to obtain heat for our houses and factories. We use the internal energy of bread (largely starch) and oxygen, by eating the former and breathing the latter, as a source of the mechanical energy required to enable our bodies to perform greater or smaller amounts of physical labor. The heat or other forms of energy obtainable from chemical actions is therefore of the most vital importance to us as human beings.

244. The Measurement of Heat. The heat produced by a chemical action is measured by carrying out the changes, with weighed amounts of the materials, in a vessel surrounded by water (a calorimeter — Greek, *heat measurer*). The amount of water is known, and its rise in temperature is observed with care. **Each gram of water raised one degree** represents one **calorie** of heat developed (see p. 50).

245. Thermochemical Equations. For convenience in chemistry we calculate, from the data obtained by measurement, the amount of heat (in calories) which would be developed by use of such quantities of the substances as are represented by the formulæ in the equation for the change. We can then insert the heat as one of the products of the action. Thus, when carbon burns with oxygen to give carbon dioxide, 1 g. of carbon unites with 2.67 g. of oxygen to give 3.67 g. of carbon dioxide and 8040 calories. Hence, since C stands for an atomic weight (12) of carbon, the amount of heat to be placed in the equation is 12 × 8040 (= 96,480) calories

$$C + O_2 \rightarrow CO_2 + 96{,}480 \text{ cal.}$$

Many actions absorb heat (are **endothermal**), instead of liberating it, as does the burning of carbon (**exothermal**). Thus, the dissociation of 36 g. of water vapor to free hydrogen and oxygen *absorbs* 4 × 28,800 = 115200 cal. This absorption is indicated by the negative sign preceding the number of calories:

$$2H_2O \rightarrow 2H_2 + O_2 - 115{,}200 \text{ cal.}$$

When the action is *reversible*, the heat absorbed when it goes in one direction is liberated when the action proceeds in the other direction.

$$2H_2 + O_2 \rightleftarrows 2H_2O + 115{,}200 \text{ cal.}$$

An action which absorbs heat can take place only if heat or some other form of energy is furnished. Thus, the decomposition of hydrogen chloride, by electrolysis of hydrochloric acid (p. 112), consumes electrical energy equivalent in amount to the heat given out when hydrogen and chlorine unite to form hydrogen chloride in solution:

$$H_2 + Cl_2 + Aq \rightarrow 2HCl, Aq + 78{,}800 \text{ cal.}$$

246. Exercises.

1. (a) What physical property of graphite enables it to cover the surface of a stove so effectively? (b) How does "polishing" with a brush contribute to the result? (c) Why not use paint on a stove? (d) Explain why graphite can be used as a lubricant.

2. If a metal formed the positive electrode (anode) in electrolysing sodium chloride solution, what chemical change might it undergo (p. 150), and which metals would be least rapidly attacked? What objection is there to using the latter metals in practice?

3. When one cubic meter of oxygen acts upon carbon, what volumes (at the same temperature and pressure): (a) of carbon dioxide; (b) of carbon monoxide can be obtained?

4. Make the equation: (a) for the formation of methane by union of carbon and hydrogen; (b) for the reduction of stannic oxide (SnO_2) by carbon.

5. What form of energy is delivered, and paid for as such, in all cities?

6. Make thermochemical equations for the combustion of diamond and graphite.

7. From the amounts of heat given out by the different forms of carbon, when burned, what do you infer as to the relative amount of energy in each form? Which form contains the most energy?

CHAPTER XVII.

THE OXIDES OF CARBON.

247. Carbon unites with oxygen in two different proportions, forming carbon dioxide CO_2, and carbon monoxide CO. These oxides differ very markedly in properties. They both have important, although very different, uses. Carbon dioxide is the gas which escapes from effervescent beverages (soda water, beer, and champagne) and immense quantities of it are used in making the carbonates of sodium. Carbon monoxide is less familiar, but very important as a constituent of fuel and illuminating gases, and as the substance directly responsible for the reduction from the ores of all the iron and steel so freely used for rails, structural iron. and innumerable other articles.

CARBON DIOXIDE.

248. Occurrence. Carbon dioxide is found in nature issuing from the ground, especially in volcanic neighborhoods, and dissolved in effervescing natural waters, such as Saratoga and Vichy. It is found in the air (4 liters in every 10,000 liters of air) and in the breath (37 liters per 1000).

249. Preparation. 1. Carbon dioxide is most easily prepared in the laboratory by the action of *an acid* such as hydrochloric acid upon a *natural carbonate* like calcium carbonate (marble or limestone). The action occurs in two stages. The first is a double decomposition, such as all acids and salts exhibit when brought in contact with one another:

$$CaCO_3 + 2HCl \rightleftarrows CaCl_2 + H_2CO_3.$$

The calcium chloride $CaCl_2$ remains dissolved in the water contained in the hydrochloric acid. The carbonic acid H_2CO_3 is unstable, however, and immediately dissociates into water, which remains, and carbon dioxide gas which escapes:

$$H_2CO_3 \rightleftarrows H_2O + CO_2 \uparrow$$

The apparatus used is similar to that employed in making chlorine (Fig. 38, p. 108).

2. For commercial purposes the carbon dioxide is either used as it is produced, or else it is compressed into wrought-iron cylinders and shipped in the form of a liquid. Three sources of such commercial carbon dioxide are in use:

When *carbon*, for example in the form of coke, *is burned* with a plentiful supply of air, all the carbon is converted into carbon dioxide.

$$C + O_2 \rightarrow CO_2.$$

Since, however, there are four volumes of nitrogen to one of oxygen in the air, this carbon dioxide is diluted with nitrogen in the same proportion. The gases must therefore be separated by leading them through potassium carbonate solution, which absorbs the carbon dioxide:

$$CO_2 + H_2O \rightleftarrows H_2CO_3 + K_2CO_3 \rightleftarrows 2KHCO_3.$$

The bicarbonate of potassium $KHCO_3$ thus produced is subsequently decomposed (see § 475).

3. *Calcium carbonate* (limestone) $CaCO_3$, or, more easily, magnesium carbonate (magnesite) $MgCO_3$, *may be decomposed* by heating in a kiln:

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow$$
$$MgCO_3 \rightarrow MgO + CO_2 \uparrow$$

In the former case the quicklime (CaO), which is formed at the same time, is a valuable product also.

4. Carbon dioxide is *liberated in fermentation*, and so is collected from the vats in which beer is brewed (see § 290).

250. Physical Properties. Carbon dioxide is a *colorless, odorless,* almost *tasteless* gas. As the molecular weight ($CO_2 = 44$) shows, it is *one-half heavier than air.* Its greater specific gravity may easily be shown by pouring it from one jar into another, or into a beaker placed on one pan of a balance with an equipoise of shot on the other pan. It is much more soluble in water than is air. One volume of water at 15° *dissolves* an equal volume of the gas. At two atmospheres pressure, two volumes are dissolved, at three atmospheres, three volumes. Pure water, charged at 3 or 4 atmospheres pressure, is known as **soda water.** Effervescent waters, such as Selters and Vichy, contain dissolved salts in addition.

The gas can be *liquefied* at any temperature below 31.1°. At 20° the pressure required is 60 atmospheres and this is therefore the pressure in a cylinder of liquid carbon dioxide at that temperature. To withstand the pressure very massive cylinders are required, and they weigh, when empty, about twice as much as does the liquid they will hold when full.

When liquid carbon dioxide is allowed to run from a cylinder into a cloth bag (non-conductor of heat), the rapid evaporation of a part of the liquid consumes so much heat that the rest of the liquid freezes to a snow-like mass of *solid carbon dioxide.* In the laboratory this solid is used as a cooling agent, being mixed with ether or benzine to secure closer contact with the object to be cooled.

251. Chemical Properties — Stability. 1. Carbon dioxide is *very stable* (only 1.8 per cent dissociated at 2000°), and so, although it contains much oxygen, it will not support combustion. Magnesium or aluminium powder (see activity list, Appendix V), however, will burn when placed on a cake of solid carbon dioxide and set on fire with burning magnesium ribbon:

$$2Mg + CO_2 \rightarrow 2MgO + C.$$

The gas extinguishes burning wood, oil, or candles, and 15 to 16 per cent of it in air is sufficient to extinguish ordinary combustibles. For this reason some **fire extinguishers** contain a dilute solution of bicarbonate of sodium ($NaHCO_3$, § 252) and sulphuric acid.

$$2NaHCO_3 + H_2SO_4 \rightleftarrows Na_2SO_4 + 2H_2CO_3$$

$$\text{or } 2Na^+ + 2HCO_3^- + 2H^+ + SO_4^= \rightarrow 2Na^+ + SO_4^= + 2H_2CO_3$$

$$2H_2CO_3 \rightarrow 2H_2O + 2CO_2 \uparrow$$

When the instrument is inverted, these materials are mixed, and water and carbon dioxide are forced out by the pressure of the gas. Disused wells and excavations should be tested with a lighted candle before being entered, since a proportion of carbon dioxide, slightly larger than the 15 per cent which extinguishes a candle, will cause suffocation.

252. Chemical Properties — Carbonic Acid. 2. Carbon dioxide, when dissolved in water, *combines* in part *to form carbonic acid:*

$$H_2O + CO_2 \rightleftarrows H_2CO_3.$$

The gas is therefore often called the **anhydride** (Greek, *without water*) of carbonic acid. The solution has all the properties of an acid, although, as the acid is very little ionized (p. 138), it exhibits them rather feebly. It tastes slightly sour, turns blue litmus faintly red, and neutralizes bases. The last action is easily shown by shaking the gas with limewater (solution of calcium hydroxide, a base):

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 \downarrow + 2H_2O.$$

The carbonate of calcium is precipitated and the liquid becomes milky in appearance. This action is used by sugar refiners for removing the lime employed in purifying the sugar. Because of its entering into double decomposition to give carbonates, manufacturers of white lead (carbonate of lead) also employ carbon dioxide. The same property is utilized in making bicarbonate of sodium and washing soda (carbonate of sodium, §§ 460–4).

Since the molecule of carbonic acid (H_2CO_3) contains two atoms of hydrogen, either one or both of these atoms may be replaced by a metal — the acid is **dibasic.** Thus we may have sodium carbonate Na_2CO_3, or its hydrate, washing soda $Na_2CO_3,10H_2O$, and also sodium bicarbonate (baking soda, sodium-hydrogen carbonate) $NaHCO_3$ (see §§ 357, 460, 464).

3. The most marvellous chemical action into which carbon dioxide enters is perhaps the most useful to mankind, and at the same time the one least understood. This is the action by which *plants use the gas as food.* This action is so important that the last section of the present chapter is devoted to it.

CARBON MONOXIDE.

253. Preparation. Carbon monoxide CO is most easily prepared in the laboratory by *heating formic acid* (or sodium formate, a white crystalline solid) with concentrated sulphuric acid. The latter combines with the water, but is not otherwise changed:

$$HCO_2H \rightarrow CO + H_2O.$$

When coke, or any form of *carbon burns with a limited supply of air* or oxygen, the same gas is produced:

$$2C + O_2 \rightarrow 2CO.$$

The gas therefore rises from the surface of a coal fire, sometimes escaping unburned, but often burning with a blue flame above the coal.

254. Producer Gas and Water Gas. When air is used with the coke, the mixture of carbon monoxide (33 per cent) with nitrogen (66 per cent) obtained is called **producer gas.** It is combustible, and is used in industrial establishments for heating and to drive gas engines for power.

Commercially, large amounts of carbon monoxide, mixed with hydrogen (**water gas**), are manufactured by *blowing steam over white hot coke* or anthracite:

$$C + H_2O \rightarrow CO + H_2 - 28{,}300 \text{ cal.}$$

The coke is first set on fire in a brick-lined cylindrical structure and brought to vigorous combustion by blowing in air for ten minutes. Then steam is substituted for the air.

The interaction, as the equation shows, takes place with absorption of heat. Hence, by the end of about five minutes, the coke has become too cool. It is then necessary to turn the steam off and to turn the air on again, and so on alternately. The mixture of carbon monoxide (40 to 50 per cent) and hydrogen (45 to 50 per cent), containing also some carbon dioxide (4 to 7 per cent), nitrogen (4 to 5 per cent), and oxygen (1 per cent), is known as **water gas.** It is almost wholly combustible, burning with a blue flame, and is used as a source of heat and, by driving internal combustion engines, to furnish power. It is used also in manufacturing illuminating gas (see § 271).

If both air and steam are driven *together* over the burning coke, the air enables the coke to burn continuously, and a fuel gas which is a cross between producer gas and water gas is obtained.

Fuel gases are employed on a large scale in steel works, and other industrial plants. They give a uniform and easily regulated heat, they leave no ash, and their use involves no labor for stoking.

255. Physical Properties. Carbon monoxide is a *colorless*, *odorless*, and *tasteless* gas. It is *a little lighter* than air (mol. wt. 28), and is very slightly *soluble* in water. It is one of the gases which are most difficult to *liquefy* (p. 97), and its boiling-point, when liquid, is −190°, close to that of liquid air.

256. Chemical Properties. When set on fire, the gas *burns* in air or oxygen with a blue flame. Carbon dioxide is formed, and the presence of the latter may be shown with lime-water (p. 161):

$$2CO + O_2 \rightarrow 2CO_2.$$

On account of this property, carbon monoxide *reduces* the oxides of the less active metals, such as those of iron and of the metals below iron in the order of activity (Appendix V). Commercially, the ores of iron are reduced by this gas (essentially producer gas) in the blast furnace. The oxides of the metals above iron are not reduced.

257. Physiological Properties. The gas is an active poison, and 1 volume in 100,000 volumes of air produces symptoms of poisoning, while one volume in 750 to 800 volumes produces death in about thirty minutes. The gas combines with the hemoglobin of the blood corpuscles, forming a stable compound, and thus preventing the absorption of oxygen by the blood (p. 30). This gas is the chief poisonous substance in illuminating gas. The poisonous effect of tobacco smoke, particularly when inhaled, is due to the carbon monoxide produced by the necessarily incomplete combustion.

When the damper of a stove is almost closed, the carbon monoxide rising from the surface of the fire (§ 253) does not escape freely into the chimney, and is apt to find its way, through the crevices, out into the room. In such circumstances, if the room is not well ventilated, a poisonous proportion of the gas may easily be reached.

CARBON DIOXIDE AS PLANT FOOD.

258. How the Plant Feeds. The walls of the cells which form the frame-work of a plant are made of cellulose $(C_6H_{10}O_5)_y$. In the cells, especially in certain parts of the plant, granules of starch $(C_6H_{10}O_5)_x$ are found. These substances differ in properties, although they have the same composition. The plant contains also protoplasm and proteins. Now all these substances contain carbon, hydrogen, and oxygen, and plant food must furnish these elements. Hence, in addition to large quantities of water ascending from the soil through the roots and stem, and sufficient amounts of compounds of nitrogen, potassium, and phosphorus, all plants require an abundant supply of carbon in absorbable form. This carbon is practically all taken up by plants in the form of atmospheric carbon dioxide. It is admitted through minute openings (stomates), situated mainly in the surface of the leaves.

259. The Reaction Involved. Comparison of the formulæ of carbon dioxide CO_2 and of any plant substance, like starch $(C_6H_{10}O_5)_x$, shows at once that the latter contains a far smaller proportion of oxygen, relatively to the amount of carbon, than does the former. Hence, during the digestion or assimilation of the carbon dioxide by the plant, this compound must be *reduced*. In point of fact, the chlorophyll (green matter) and protoplasm in the leaves act upon the carbon dioxide, causing oxygen to be liberated:

$$6CO_2+5H_2O \rightarrow C_6H_{10}O_5+6O_2 \uparrow$$

This action goes on only in the sunlight. The steps by which sugar, starch, and cellulose are manufactured by the plant out of water and carbon dioxide, are not well understood. But the liberation of the oxygen is easily shown by placing a green plant under water in a jar, and setting the jar in the sunlight (Fig. 49). Bubbles of gas appear

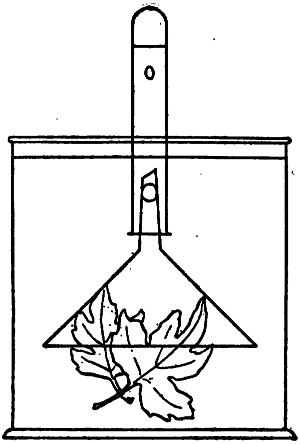

Fig. 49

on the leaves, grow larger, and then detach themselves and rise to the top. The gas relights a glowing splinter of wood, and is pure oxygen.

260. The Thermochemistry of the Reaction. In the combination of carbon and oxygen, during combustion of wood or coal, much heat is liberated. Hence, when oxygen is taken out of carbon dioxide again, heat or energy in some form must be *supplied*. *When this takes place in a plant*, the energy is evidently furnished by the sunlight, for the action proceeds more slowly in the shade, and ceases in the dark.

The energy required can be measured, and may be expressed in calories. The energy required to produce one formula-weight of cellulose ($C_6H_{10}O_5 = 6 \times 12 + 10 \times 1 + 5 \times 16 = 162$ g.) is 671,000 calories. The whole may be represented in a rough equation, in which the unknown intermediate steps are left out, and only the starting substances and the final products are shown:

$$6CO_2 + 5H_2O + 671{,}000 \text{ cal.} \rightarrow C_6H_{10}O_5 + 6O_2.$$

261. Source of the World's Energy. The energy that does the world's work comes mainly from two sources, namely water power and the combustion of wood, or of coal (which is fossil wood). The water comes from vapor, generated by the *sun's heat*, condensed as rain, and collected in lakes or reservoirs. The source of the energy of coal or wood is a little less obvious. When wood (which is largely cellulose) burns, it gives carbon dioxide, water, and heat. In fact, its combustion is represented in the above equation, *when the equation is read backwards*. Thus the sunlight, working through the machinery of the plant, takes the carbon dioxide and water, furnishes the energy (as light), and gives us wood and oxygen. And the wood and oxygen, when burned, give us back the original substances, and the equivalent of the original energy in the form of heat. Hence, our other main source of energy turns out to be the same as the first — the sun's rays — although the route by which the energy comes to us is a little less direct.

If, instead of *burning* the starch of the plant, *we consume it as food*, it goes through a *series* of changes instead of only *one*. But the end products are the same, namely, carbon dioxide and moisture issuing from our lungs, and heat and other forms of energy such as are developed in living organisms. Thus, whether we use our muscles, a steam engine, or a water-wheel to do work, sunlight is in each case the ultimate source of energy employed.

262. Exercises.

1. Make equations for: (a) the action of sulphuric acid upon calcium carbonate; (b) carbon dioxide on sodium hydroxide solution (p. 161); (c) the burning of aluminium in carbon dioxide.

2. From the fact that the molecular weight of carbon dioxide is 44, how do we infer that it is one-half heavier than air?

3. Why does soda water remain quiescent in the closed bottle, and why does it effervesce when the bottle is opened?

4. What may be the sources of carbon dioxide in disused cellars and excavations?

5. Name the variety of chemical change (§ 147) to which belongs the reaction shown in each equation in this chapter.

6. Assuming that air contains oxygen and nitrogen in the proportion of 1 : 4 by volume, what are the theoretical proportions of carbon monoxide and nitrogen in producer gas?

7. (a) What volume of water gas is produced from each liter of steam, and (b) what is the proportion of the component gases in the product? (c) What impurities should you expect to find in water gas? (d) How should you attempt to separate the components of water gas (see § 315)?

8. Why is water gas an especially valuable source of heat when high temperatures are required (see § 245)?

9. Make a list of metals the oxides of which would be reduced by carbon monoxide.

10. In what relative volumes are carbon dioxide used and oxygen produced by a plant?

CHAPTER XVIII.

COMPOUNDS RELATED TO PETROLEUM. FLAME.

263. Petroleum introduces us to the compounds of carbon and hydrogen, called by chemists the hydrocarbons. Many scores of these are known, and a number occur in nature. Thus, the natural oil, petroleum, is a mixture of hydrocarbons. To understand its treatment and uses, we must consider first the nature of its components.

264. The Hydrocarbons. The following list contains the names, formulæ, and boiling-points of seven of the simplest hydrocarbons and of two others.

Methane CH_4	b.-p.	−164°	Hexane C_6H_{14}	b.-p.	71°
Ethane C_2H_6		−89.5°	Heptane C_7H_{16}		99°
Propane C_3H_8		−37°	Hexadecane $C_{16}H_{34}$		287.5°
Butane C_4H_{10}		+ 1°	Hexadecane $C_{16}H_{34}$	m.-p.	18°
Pentane C_5H_{12}		35°	Pentatriacontane $C_{35}H_{72}$	m.-p.	74.7°

After the first four, the names are based on the Greek numerals corresponding to the number of carbon atoms in the molecule. Thus heptane is followed by octane C_8H_{18}, nonane C_9H_{20}, decane $C_{10}H_{22}$ and so forth. On comparing the formulæ, we observe that, in each, the number of units of hydrogen is equal to twice the number of carbon units plus two. The general formula is therefore C_nH_{2n+2}. The series affords a striking illustration of the law of combining weights (p. 64). We note, further, that the first four are gases at the ordinary temperature. The members of the series from pentane to pentadecane ($C_{15}H_{32}$) are liquid under ordinary conditions. From hexadecane onwards they are solids, with higher and higher melting-points.

Even this long series, the members of which have been studied up at least as far as hexacontane $C_{60}H_{122}$ (m.-p. 102°), does not include all the known hydrocarbons. Thus, a compound, to the presence of which illuminating gas largely owes its luminous flame, is **ethylene** C_2H_4. Starting with this compound, another series (C_nH_{2n}) is known, of which the molecules contain 2 atoms of hydrogen less than the corresponding compounds of the first series. There are yet other series, such as that beginning with **acetylene** $C_2H_2(C_nH_{2n-2})$, in which the proportion of hydrogen is relatively still smaller.

The ethylene, acetylene, and other series, in which the proportion of hydrogen is less than the maximum, are spoken of as **unsaturated hydrocarbons,** because the full valence of the carbon is not in use, and these compounds unite with hydrogen, chlorine, and other elements rather readily. On the other hand, the members of the first series are called the **saturated hydrocarbons.** These can take up other elements only by giving up a part of their hydrogen to make room for the new element.

All these hydrocarbons are *mutually soluble*, so that mixtures can be made in any proportion, and using any number of members of the different series.

265. Petroleum. Petroleum is a thick, greenish-brown oil. When borings are made into the oil-bearing strata, the oil either gushes up, or is pumped to the surface. Wells of this kind are in operation at Baku on the Caspian, in India, in Japan, in Ontario, and in Ohio, Pennsylvania, California, and elsewhere in North America. In the United States hundreds of miles of pipe-lines are used to transport the oil, with the aid of force pumps, to the refineries, and in 1912 nearly 220 million barrels (42 gal. each) were produced. The world's production in 1912 was 350 million barrels.

266. Oil Refining. The natural oil is a complex mixture, and the components are *partially* separated in order to get products suitable for various purposes. The separation is carried out by distillation. The components of lower boiling-point come off first. Then the remaining oil is chilled and a quantity of the solid members of the series ($C_{22}H_{46}$ to $C_{28}H_{58}$) crystallizes in flakes (solid **paraffin**) and is separated by filtration. The unsolidified oil is distilled further to get the components of intermediate boiling-point. The residue is used for lubricants and for fuel. The various products are still mixtures, but contain only compounds lying close together in the series. Some of the products, together with their main components and uses, are as follows:

Name.	Main components.	B.-P.	Uses.
Petroleum ether ..	Pentane, hexane...	40°– 70°	Solvent, gas-making
Gasoline..........	Hexane, heptane...	70°– 90°	Solvent, fuel
Naphtha..........	Heptane, octane...	80°–120°	Solvent, fuel
Benzine...........	Octane, nonane....	120°–150°	Solvent
Kerosene.........	Decane-hexadecane	150°–300°	Illuminating oil

Vaseline, $C_{22}H_{46}$ to $C_{23}H_{48}$, is separated in some refineries. **Solid paraffin** is employed for waterproofing paper, as an ingredient in candles, and in making chewing gum.

Asphalt, a natural mixture of the solid hydrocarbons, found particularly in Trinidad, is used in road-making.

267. Natural Gas: Methane CH_4. Natural gas is obtained from wells, tapping strata close to those which contain petroleum, and in the same localities. It often issues under very high pressure. It owes its combustibility to its chief component (over 90 per cent), **methane** CH_4. It is largely used as a fuel in the regions in which it is found and, in the United States, the annual value of the gas so consumed is estimated at nearly $73,000,000 (1910). The same gas ("fire-damp") issues from many coal seams, and forms explosive mixtures with the air of mines. It rises to the surface when stagnant pools containing decomposing vegetable matter are stirred ("marsh-gas").

268. Acetylene C_2H_2. A mixture, containing acetylene, is formed when any hydrocarbon is heated strongly (§ 270), air being excluded. Acetylene is prepared by the action of water on calcium carbide (p. 153):

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \uparrow$$

Calcium hydroxide (slaked lime) remains. The gas *burns* with a flame even more luminous than that of ethylene. It is therefore made in generators by the foregoing action for use on automobiles and for lighting buildings remote from a public supply of illuminating gas. Acetylene tanks, which are also in use, contain acetylene dissolved, under high pressure, in acetone.

269. The Acetylene Blowpipe or Torch. Acetylene decomposes, when heated, with *liberation* of heat:

$$C_2H_2 \rightarrow 2C + H_2 + 53{,}100 \text{ cal.}$$

When acetylene burns with oxygen, therefore,

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O,$$

we obtain not only the heat due to the combustion (p. 156) of the carbon (4 × 96,480 cal.) and of the hydrogen (4 × 28,800 cal.) but also the heat due to the decomposition of the gas (2 × 58,100 cal.). The temperature of the flame is, therefore, the highest that can be reached by the combustion of any easily obtainable gases. The oxy-acetylene flame, produced by means of a suitable burner (Fig. 22, p. 45), the gases being furnished from small, portable tanks, is now used for cutting metals. Such a flame will melt its way through a 6-inch shaft of steel, or a heavy steel plate several feet wide, in less than one minute, cutting the object in two. Steel buildings have been taken apart rapidly by this device.

Blau gas and **oil gas,** mixtures of hydrocarbons made by "cracking" (see next two sections) heavy oils, are now largely displacing acetylene for uses like those just mentioned. They give flames which are almost as effective, and are more easily controlled. Even the oxy-hydrogen torch is remarkably efficient, when applied to the same purposes.

270. Chemical Properties of the Hydrocarbons. The hydrocarbons, whether pure or in solution, show *no conductivity* for electricity. In general, they have none of the chemical properties of acids, bases, or salts, and therefore do not enter into double decompositions with substances of these classes. The saturated hydrocarbons are in fact *quite indifferent* to the presence of most chemical reagents.

The *unsaturated* hydrocarbons act chiefly by combining with hydrogen, the halogens, and some acids:

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \text{ (ethylene chloride).}$$

All the hydrocarbons *burn* with oxygen or air to form carbon dioxide and water:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O.$$
$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O.$$

The water can be shown by its condensation on a cold vessel held over the flame. The carbon dioxide gives a precipitate of calcium carbonate (p. 161) when the gases rising from the flame are drawn through lime-water.

All the hydrocarbons, when *heated strongly* (air excluded), *decompose* or **crack.** They usually lose a part of their hydrogen and become unsaturated. These of high molecular weight break up to give a mixture of hydrocarbons of low molecular weight. Ethylene C_2H_4, for example, is produced in large amounts by heating the higher members of the series to a red heat. On the other hand, the lower members of the series, when heated, often give compounds of higher molecular weight. Thus, methane gives ethylene and acetylene, along with hydrogen,

$$2CH_4 \rightarrow C_2H_4 + 2H_2.$$
$$2CH_4 \rightarrow C_2H_2 + 3H_2.$$

At a white heat all the hydrocarbons decompose into hydrogen and free carbon:

$$CH_4 \rightarrow C + 2\,H_2.$$

271. Carburetted Water Gas. To fit water gas, essentially $H_2 + CO$ (p. 163), which burns with a pale blue flame, for public service as an illuminating gas, unsaturated hydrocarbons, and particularly ethylene C_2H_4, which burn with a highly luminous flame, must be added. The water gas is passed through a tower, filled with strongly heated brick on which oil is continually sprayed. Mixed with the vapor of the oil, the gas goes into the "superheater" where, at a higher temperature, the decomposition into unsaturated hydrocarbons (**cracking**) takes place. The gas is then cooled and washed to remove the condensible hydrocarbons, which would otherwise collect in the service pipes, with resulting waste of combustible material as well as obstruction in the delivery of the gas. A typical carburetted water gas has the composition: Illuminants (largely ethylene) 16.6 per cent; heating gases — methane 19.8 per cent, hydrogen 32.1 per cent, carbon monoxide 26.1 per cent; impurities (nitrogen and carbon dioxide) 5.4 per cent.

272. Sources of Gasoline. The demand for gasoline (petrol) for use in automobiles and motor launches has recently become greater than the natural supply of the more volatile components of the natural oil. Two new sources of gasoline have been found. One plan is to crack the heavier hydrocarbons by heat in such a manner as to get a fair yield of the saturated compounds boiling between 70° and 90°. The other is to apply pumps to the disused gas wells, from which natural gas no longer issues, and thus, by creating a vacuum, to promote the evaporation of the volatile part of the liquids remaining in the strata. The vapor so obtained in then condensed.

FLAME.

273. We have encountered a variety of flames, from the simple one of hydrogen burning in air to the more complicated case of the luminous flame of ethylene or acetylene. The subject will now repay a somewhat closer study.

274. The Simple Flame. The flame of hydrogen (giving water), or of carbon monoxide (forming carbon dioxide) is very simple in structure (Fig. 50). We find that there is a tapering column of unburnt gas in the interior, surrounded by a layer of hot gas — the flame itself. The flame is therefore a hollow cone. That the flame is hollow is easily shown by holding a wooden match across it. The match is charred at the two points at which it crosses the flame, and remains unheated in the middle. These flames are simple, because only one chemical change occurs in them. The flames are rather large, because sufficient oxygen to burn all the gas does not reach the latter at once, and the gas travels upwards and diffuses outwards a certain distance before being all consumed.

Fig. 50

If oxygen is substituted for air, by lowering the jet into a jar of that gas, the flame becomes much smaller. In the absence of atmospheric nitrogen, there is now five times as much oxygen within a given range of the center of the jet as before. This chemical union, like any other, proceeds more rapidly with an increase in the concentration of the interacting substances. It is therefore completed before the gas has time to diffuse very far from the opening of the jet.

275. The Candle Flame. A candle is made of a mixture of paraffin and stearic acid (a compound of carbon, hydrogen with some oxygen, made from fat). When it burns, the whole phenomenon is vastly more complicated than the burning of hydrogen. The following are some of the stages in the process, which is operated by the flame's own heat. To start with, the wax is melted and ascends the wick by capillary action. This is merely a physical phenomenon. Then the chemical changes begin. (1) The melted compounds of carbon are decomposed by the heat (cracked, p. 172), being turned into more volatile compounds and gases which occupy the central hollow of the flame. (2) The compounds forming the gases and vapors are further decomposed at a white heat, giving free carbon and hydrogen (p. 173). (3) All the materials finally reach a sufficient supply of oxygen and are burned to water and carbon dioxide. There are thus three chemical changes, each of which takes place in a definite region that can be observed by the eye (Fig. 51). The formation of the gases from the melted wax (without gas, there would be no flame) takes place in the dark central region where there is no oxygen. The carbon is set free and glows brilliantly in the luminous cone that surrounds the gas and extends far above it. The final combustion occurs in a fainter cone of flame covering the whole exterior.

Fig. 51

That there is unburnt gas (produced by decomposition of the wax) in the center is easily shown by inserting a narrow tube, through which some of the gas will ascend. The free carbon in the luminous zone will show its presence by blackening a cold dish placed across the flame.

276. Ordinary Illuminating Gas. The candle is a miniature gas factory. It makes its own gas, and burns it as well. It is more convenient and economical, however, to leave the manufacture of the gas to a public corporation, which distributes it in pipes. In large cities the gas is usually carburetted water gas (p. 173). In many cases, however, coal gas, made by distilling coal (§ 577), is the kind delivered. In the United States, in 1909, the quantities delivered by public service companies, expressed in billions of cubic feet were: water gas, 80; coal gas, 20; mixtures of both, 40.

The luminosity of the flame depends upon the complete decomposition of the hydrocarbons (particularly, the ethylene) in the gas. This decomposition with liberation of carbon, is brought about, as in the candle, by the heat of the surrounding mantel of flame.

277. Lampblack. When an iron vessel, cooled by a stream of water circulating through it, is suspended in the flame of natural gas or burning petroleum, the carbon (soot) is deposited on the vessel. By rotating the latter, the soot can be continuously scraped off by a stationary piece of metal. The product, **lampblack,** being very finely divided carbon, is used in making printers' ink, India ink, and black varnish.

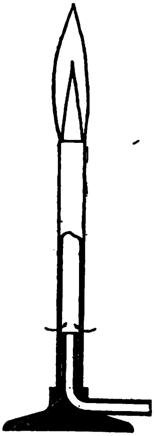
Fig. 52

278. Non-luminous Gas Flames. When the gas is to be used for heating, the complete combustion of the gas, without any intermediate liberation of free carbon, is desirable. This is achieved in the Bunsen burner (Fig. 52) by admitting air at the bottom of the burner, in such a way that the air mixes with the gas before the latter reaches the flame. The air cools the middle zone of the flame, so that at this point the temperature required for dissociating the ethylene, and liberating carbon, is not reached. The oxygen in the air plays no part — mixing carbon dioxide or pure nitrogen with the gas has exactly the same effect. A flame of this kind is non-luminous.

Although *the middle zone* of the non-luminous flame is cooler than that of the luminous flame, the *average temperature* of the flame as a whole *is higher*. This is the case because the same total amount of heat is liberated in both cases, but the non-luminous flame as a whole is *smaller* in size.

The Bunsen type of burner, placed in a horizontal position (Fig. 53), is used in the ordinary gas cooking range. As with the Bunsen burner, some care is required to get good results. The holes which admit the air to the mixer must be kept clear of obstructions, as otherwise luminous flames are produced, smoke and soot are formed, and less heat is generated. The size of the openings must be adjusted, as the admission of too much air causes the flame to flash down the burner, and set fire to the gas within the mixer.

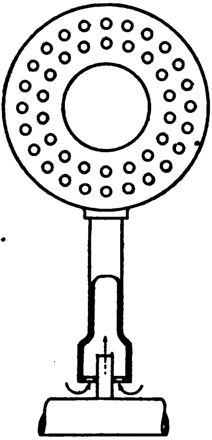
Fig. 53

279. Flames with Incandescent Mantels. When gas is burned in a Bunsen burner, a bright light may still be obtained from the flame. This is managed by suspending in the flame a structure ("mantle") made of the oxides of thorium (99 per cent) and of cerium (1 per cent). That these oxides could cohere well enough to withstand ordinary treatment, could give out a brilliant, white light when thus heated, and could be manufactured at a price consistent with use in any household, was discovered by Auer von Welsbach. For the same amount of gas passing through the meter the Welsbach lamp gives four times as much light as an ordinary burner.

280. Exercises.

1. When vegetable matter decays in the air the carbon it contains is finally all turned into carbon dioxide. When the same matter decays under water, it gives methane (p. 171). Explain the difference in the result.

2. (a) Given a flame of hydrogen burning in a jar of air, what would be the effect on the flame of lowering the pressure of the air by means of an air pump? (b) What would be the effect on the average temperature of the flame? (c) How about the heat produced by burning 1 g. of hydrogen in each case? (d) What differences would be observed in using an alcohol lamp at the bottom and on the top of a high mountain?

3. (a) In the candle or gas flame, what is the source of the light? (b) Why does such a flame become smoky when placed in a draft?

4. What is the density (air = 1) of (a) methane, (b) ethylene?

CHAPTER XIX.

STARCH AND COMPOUNDS MADE THEREFROM.

281. We have already seen (p. 165) how the plant takes carbon dioxide from the air, and water from the ground, and manufactures starch $C_6H_{10}O_5$ out of them. All the higher plants carry on this important process on a huge scale. Of these plants many, such as wheat, oats, maize (corn) and potatoes, are cultivated for use as food, and the starch is one of the chief foodstuffs that they contain. Furthermore, from starch we can readily make sugar, alcohol, vinegar and other familiar substances. Starch, in fact, introduces us to a much greater variety of organic compounds than does petroleum.

282. Starch $(C_6H_{10}O_5)_x$. Starch is found in plants in little *colorless granules* of various rounded shapes (Fig. 54) which may readily be seen under the microscope. These granules are massed in large numbers in the ears of wheat and oats, in the tubers of potatoes, in the grains of maize (corn) and in peas and beans. Even in the leaves they can be seen immediately after the plant has been exposed to sunlight. They gradually disappear from the leaves in the dark. They can be recognized, not only by their appearance, but, without a microscope, by the **iodine test.** When a drop of a potassium iodide solution, rendered brown by the addition of a little free iodine, is placed on the leaf or other part of the plant, the granules of starch become *blue* while the other parts are not affected.

Fig. 54

283. Preparation of Starch. If flour, which is made by grinding wheat, and is three-fourths starch, is placed in a muslin bag and kneaded under water, the granules of starch are washed out and render the water milky. After a time the granules settle and the water can be poured off. Starch is manufactured by washing disintegrated potatoes (in Europe) or maize (in America) on sieves, and collecting and drying the white powder deposited in the water used for the washing.

Starch is *not soluble* in water. If it be boiled with water, however, the granules swell and break, and the starch becomes finely diffused through the water, forming a clear liquid. With little water, a sort of transparent jelly is produced. When the liquid is poured through a filter, a large part of the starch goes through the paper as if it were truly dissolved. Such a liquid is called a **colloidal suspension.** Imitation solutions like this are constantly met with in using complex organic compounds such as enter into jellies, glues, soaps, and the juices of the bodies of animals. Even inorganic substances, of the insoluble class, give such suspensions. A description of their peculiarities must be reserved until later (§ 501).

The colloidal suspension of starch turns *blue throughout* when the iodine solution is added to it.

The colloidal suspension of starch is *used* in the laundry, for stiffening white goods. Glucose is manufactured from it.

284. Glucose $C_6H_{12}O_6$ from Starch. When starch is boiled with water, to which a few drops of an acid (contact agent), such as hydrochloric acid, have been added, the liquid, after neutralization of the acid, is found to be sweet in taste. A kind of sugar, **glucose** $C_6H_{12}O_6$, can be obtained in crystals by evaporation. The crystals are sold as "brewers' glucose," and the syrup ("corn-syrup," if maize is the source of the starch) is sold as "confectioners' glucose" for making candy and for preserving fruits.

To understand the action, we must note that, although the formula $C_6H_{10}O_5$ represents the composition of starch, its molecular weight (the value of which is unknown) is very large, say $(C_6H_{10}O_5)_x$. The water decomposes the large molecules and combines with the material:

$$(C_6H_{10}O_5)_x + x\,H_2O \rightarrow x\,C_6H_{12}O_6.$$

The action is an **hydrolysis** (Greek, *decomposition by water*).

Glucose is known also as **dextrose,** and as **grape sugar.** Brownish crystalline granules found in dried grapes (raisins) are mainly composed of it. When pure, it is almost colorless. It *reduces* cupric hydroxide, in Fehling's solution (see § 647), to hydrated cuprous oxide.

285. The Sugars. The common sugars are divided into two classes. Two sugars, having the same formula, $C_6H_{12}O_6$, but different properties, are called **monosaccharides.** Other sugars, having usually twice as many carbon units in the formula, $C_{12}H_{22}O_{11}$, are called **disaccharides.** The sugars we have occasion to mention are the following:

Monosaccharides:	**Glucose** (dextrose or grape sugar) $C_6H_{12}O_6$.
	Fructose (fruit sugar) $C_6H_{12}O_6$.
Disaccharides:	**Sucrose** (cane-sugar, beet-sugar, saccharose) $C_{12}H_{22}O_{11}$.
	Maltose (formed by action of malt on starch) $C_{12}H_{22}O_{11}$.
	Lactose (milk-sugar, found only in animals) $C_{12}H_{22}O_{11}$.

286. Carbohydrates. Since starch and the sugars are freely changed, one into another, they form one class, the car-

bohydrates. The word refers to the fact that they usually contain hydrogen and oxygen in the proportions required to form water, and are, therefore, in a sense, hydrates of carbon.

287. Sucrose or Cane-Sugar $C_{12}H_{22}O_{11}$. A number of plants, besides producing starch, are able also to convert carbon dioxide and water into sucrose $C_{12}H_{22}O_{11}$. The sugar-cane and the beet produce exceptionally large amounts of this sugar, which is the one commonly used as table sugar. Maple sugar, obtained by evaporating the sap of the tree, is composed mainly of the same substance.

The sugar-cane forms stalks from ten to twelve feet high. The juices are extracted by crushing the plants between rollers. The liquid is evaporated in closed pans. A vacuum maintained in the pans permits the boiling of the solution at a low temperature (about 65°) and prevents the decomposition of a part of the sugar which would otherwise occur. When the syrup cools, the sugar crystallizes and the crystals are freed from the liquid in centrifugal machines. The crystals are brown in color. At the sugar refinery they are dissolved, and the solution is passed through a column of bone charcoal. This absorbs the coloring matter, and the filtrate is once more evaporated and allowed to crystallize. Refined cane-sugar has a faint yellow tint, and a small amount of ultramarine is added to cover up this tint, and give the white appearance which is popularly connected with purity in sugar.

The sugar beets, which contain 16 per cent or more of cane-sugar, are sliced and steeped in water to extract the sugar. The liquid contains gummy material in colloidal suspension. This is coagulated and precipitated by adding "milk of lime" (calcium hydroxide $Ca(OH)_2$ suspended in water) and boiling. Carbon dioxide is then passed through the solution to precipitate the excess of lime:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O.$$

The solution is decolorized with charcoal and evaporated to crystallization in the same way as is the extract from the sugar-cane.

288. Properties of Sucrose. Sucrose *crystallizes* in four-sided prisms, the form of which is seen in "rock-candy." It *melts* at 160°. It does not reduce Fehling's solution (§ 284). When heated to 200 to 210° it begins to decompose, slowly losing water and leaving a brown, soluble mass called **caramel,** used in coloring whisky and soups.

When boiled with water, to which a trace of an acid (contact agent) has been added, it is *hydrolyzed* (p. 181), giving a mixture of the two monosaccharides, glucose and fructose:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6.$$

This mixture of glucose and fructose is called **invert sugar** and is found in many sweet fruits and in honey. Each sugar interferes with the crystallization of the other, by lowering the freezing-point (p. 91), and so invert sugar is added in making "fondant" candy and candy that is to be "pulled," both of which are intended to remain soft for a longer or shorter time. With the same object in view, vinegar, lemon juice, or cream of tartar is added to a syrup made from cane-sugar, in order that the acid contained in them may produce some invert sugar and so give a less crystallizable mixture. Prolonged heating has the same effect.

289. Enzymes. Yeast belongs to a low order of plants and consists of minute cells of microscopic size. Its value lies in the fact that, while growing and multiplying, it secretes within each cell small amounts of two very active chemical substances which are dissolved in the cell contents. These substances are known as **zymase** and **invertase** (more strictly,

sucrase, meaning an enzyme that splits sugar), and belong to the class of organic materials called **enzymes**. They produce remarkable chemical changes by their mere presence (contact actions).

290. Alcoholic Fermentation. When a cake of yeast, which contains the living plants, is broken into an aqueous solution of glucose (p. 181), the small amount of zymase causes the gradual decomposition of the sugar. The most favorable temperature is about 30°. Bubbles of carbon dioxide soon begin to rise to the surface, and the gas can be led off (Fig. 55) to exhibit its characteristic action (p. 161) on lime-water. At the same time alcohol C_2H_5OH accumulates in the liquid as the sugar disappears:

$$C_6H_{12}O_6 \rightarrow 2CO_2 \uparrow + 2C_2H_5OH.$$

The liquid extracted from the yeast cells works as well as does the plant itself, and dead yeast produces the change also. The live plant is employed because then only a few cells are needed to start with, and others rapidly form as the plant grows.

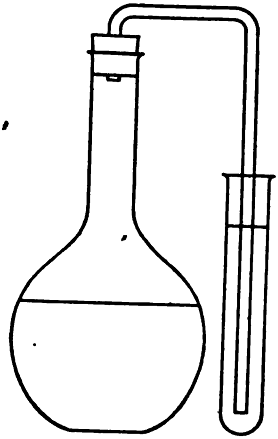

Fig. 55

Yeast will ferment fructose ($C_6H_{12}O_6$), with the same result, but more slowly. When placed in invert sugar (p. 183), therefore, it decomposes the glucose first and the fructose afterwards.

Zymase does not act upon sucrose ($C_{12}H_{22}O_{11}$). But the invertase (sucrase), which is also contained in the yeast, hydrolyzes the sucrose in the same way as does a dilute acid, giving invert sugar. The latter is then decomposed by the zymase. Hence cane-sugar in solution is decomposed by yeast into alcohol and carbon dioxide, just as is glucose, only more slowly.

In the manufacture of **wines** the glucose contained in the grape juice is fermented by a species of yeast always found on the skins.

291. Common Alcohol C_2H_5OH. This alcohol is related to ethane C_2H_6, containing an hydroxyl (OH) group in place of one unit of hydrogen. Hence, to distinguish it from other alcohols, it is named **ethyl alcohol.**

Ethyl alcohol *boils* at a lower temperature (78.3°) than water. When, therefore, the fermented liquid is distilled, the alcohol comes off first, along with comparatively little water. The stills used in distilleries give 95 per cent alcohol.

Ethyl alcohol *mixes* in all proportions with water. It does not dissolve much cane-sugar or fat, but it *dissolves* many substances which are little soluble, or are insoluble in water, such as iodine and resins. It is *used* as a solvent in making varnishes for wood and lacquers for metal, as well as plastics like celluloid, collodion, and artificial silk (§ 514). In Germany it is used for lighting and cooking.

Alcohol is *not ionized* in aqueous solution, and it does not interact with dilute acids, bases, or salts. It is, however, more active than the hydrocarbons. Thus, it is *easily oxidized*, giving, as we shall presently see, acetic acid. With acids, when water is absent, it interacts slowly (see §§ 495, 511).

There are **other alcohols,** of which those most closely related to ethyl alcohol have the general formula $C_nH_{2n+1}OH$.

292. Commercial Alcohol, Whisky, and Beer. Commercial alcohol is made from the starch of potatoes or maize. Barley, which has been allowed to sprout, and is then dried, is called **malt.** This contains an enzyme, **diastase** (more strictly,

amylase, meaning an enzyme that splits *starch*), which is able to hydrolyze starch into maltose $C_{12}H_{22}O_{11}$ (p. 181). Maltose is further hydrolyzed by yeast to form glucose, and the latter is then decomposed by the zymase into alcohol and carbon dioxide.

Whisky is made by treating the starch of rye, maize, or barley in the same way, with subsequent separation of the alcohol (whisky) by distillation. **Beer** is made similarly from various kinds of grain, particularly barley, except that the fermented liquid is not distilled.

293. Denatured Alcohol. This is alcohol to which 10 per cent of wood spirit and 0.5 per cent of benzine, or 2 per cent of wood spirit and 0.5 per cent of pyridine bases from bone oil, nauseous and poisonous substances, have been added. Pure alcohol, such as can be used in the preparation of spiritous liquors, is subject to a tax of $2.08 per gallon (costs $0.22 and sells at $2.50). Denatured alcohol, since it cannot be so used, is duty-free (in U. S. since 1907). Yet it is equally suitable for varnish-making and other industrial operations, which are thus relieved from the tax with which formerly they were burdened.

294. Acetic Acid HCO_2CH_3. This acid is the active substance in vinegar, and has many industrial uses. It is formed by the action of *mild* oxidizing agents on alcohol. (The active oxidizing agents give with alcohol only carbon dioxide and water.) Vinegar is manufactured by oxidizing alcohol with atmospheric oxygen, using a bacterium (*B. Aceti*, " mother of vinegar "), or more probably an enzyme which it secretes, as a contact agent. The dilute alcohol, in the form, for example, of " hard " cider (fermented apple juice), is allowed to trickle over shavings in a barrel. The shavings are inoculated with the *B. Aceti* by preliminary wetting with

vinegar. Holes in the sides admit a plentiful supply of air (and therefore of oxygen), to the action of which the liquid is exposed by being spread over the surface of the shavings:

$$HOC_2H_5 + O_2 \rightarrow HCO_2CH_3 + H_2O.$$

The liquid (vinegar), which issues at the bottom, contains from 5 to 15 per cent of acetic acid, besides coloring and flavoring matters derived from the fruit juices.

Pure acetic acid is prepared by distilling the vinegar repeatedly. Large amounts are obtained also from the liquid distillate, obtained by heating wood in the manufacture of charcoal. It is a colorless *liquid* which *boils* at 118° and *freezes* at 16.7°. It is a monobasic *acid.* In aqueous solution it is *slightly* ionized, the radicals being H^+ and $CO_2CH_3^-$.

There are **other acids** of the same series, the general formula of which is $HCO_2C_nH_{2n+1}$.

295. Cellulose $(C_6H_{10}O_5)_y$. This substance, named cellulose because it forms the walls of the cells, composes much of the frame-work and intricate structure of plants. We are familiar with pure cellulose in the forms of **filter paper** (see paper manufacture, § 358) and **cotton.** The latter consists of fine, hollow tubes of cellulose (see Fig. 2, p. 2), large tufts of which surround the seed of the cotton plant. **Linen** is almost pure cellulose, **wood** is largely cellulose, and **paper** pulp is practically all cellulose.

Cellulose *interacts* with very few chemical substances. It is because it thus remains unchanged, by most substances that come in contact with it, that it can be used as a filter paper. When it does undergo chemical change, it acts as if it contained hydroxyl (OH) groups, and behaves therefore chemically like an alcohol (see Chap. XXXII).

296. Exercises.

1. What inference do you draw as to the composition of tapioca, sago, and rice from the facts that they are fruits and when boiled with water and cooled give a jelly-like mass? How should you confirm your inference?

2. (a) Why does a strong solution of sugar boil at a temperature far above that of boiling water? (b) In evaporation why is the boiling-point lower in a vacuum than in air?

3. In fermentation why does not carbon dioxide appear in bubbles *at once?*

4. What determines the proportion of alcohol in a wine made from pure grape juice?

5. Write the formulæ of the acetates of potassium, and of calcium.

6. How do we ascertain that acetic acid in aqueous solution is only slightly ionized?

7. What products must be formed when paper is burned? Make the equation.

CHAPTER XX.

NITROGEN. THE ATMOSPHERE.

297. It is time now to return to the atmosphere, of which the most active component, oxygen, has already been discussed. The other chief component, nitrogen, will lead us to ammonia NH_3 and nitric acid HNO_3, both of which are of great commercial importance, and have interesting derivatives.

298. Occurrence of Nitrogen. Aside from the free nitrogen, which forms nearly four-fifths of the bulk of atmospheric air, much nitrogen is found in nature in combination. Potassium nitrate KNO_3 is formed in the soil by the action of bacteria upon animal matter, and sodium nitrate $NaNO_3$ is obtained from an immense deposit in Peru and Chile. Nitrogen is an essential constituent of an important class of organic substances, called the *proteins*, which are found in plants, particularly in the fruit, and in the muscles and other tissues of the animal body.

299. Preparation. Nitrogen may be obtained from the air by simply removing the oxygen. This nitrogen is not pure, however, as it retains about one per cent of other gases — the " inert gases " of the atmosphere. The oxygen can be removed by allowing pieces of moist phosphorus (Fig. 56) slowly to oxidize in an enclosed specimen of air. The phosphoric acid H_3PO_4 and other products of the oxidation of the phosphorus dissolve in the water.

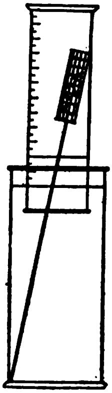

Fig. 56

Pure nitrogen can be obtained from pure compounds of nitrogen. Thus, ammonia gas may be passed over heated cupric oxide (Fig. 57), and the water removed by bubbling the gas through sulphuric acid.

Fig. 57

Skeleton: $NH_3 + CuO \rightarrow Cu + H_2O + N_2$.
Balanced: $2NH_3 + 3CuO \rightarrow 3Cu + 3H_2O + N_2$.

A steady stream of nitrogen is most easily made by heating sodium nitrite and ammonium chloride very gently along with a little water in a flask:

$$NaNO_2 + NH_4Cl \rightleftarrows NaCl + NH_4NO_2 \rightarrow 2H_2O + N_2 \uparrow$$

The double decomposition is reversible, and the first action might be expected to be only partially completed. But the ammonium nitrite NH_4NO_2 is unstable, and decomposes as fast as it is formed, so that one of the substances required to reverse the first reaction is removed, and the reversing action does not occur.

300. Physical Properties. Nitrogen is a *colorless, tasteless* and *odorless* gas. Its *density* is indicated in the formula N_2 (mol. wt. $2 \times 14 = 28$). It is very *little soluble* in water, and is one of the gases which Faraday failed to liquefy. When *liquefied* it boils at $-194°$. It can also be solidified.

301. Chemical Properties. Nitrogen is chemically a rather indifferent gas. It unites easily with a very few elements, notably some of the *most active metals*, such as calcium and magnesium. When magnesium burns in the air, the white powder which is formed contains some of the *nitride* of magnesium Mg_3N_2, along with much of the oxide:

$$2Mg + O_2 \rightarrow 2MgO.$$
$$3Mg + N_2 \rightarrow Mg_3N_2.$$

The presence of the nitride may be shown by the odor of ammonia, given off when the ash is moistened with water:

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3 \uparrow$$

The compounds with oxygen, such as NO and HNO_3, and with hydrogen, such as NH_3, are of immense commercial value, but, not being very stable, they are formed only in traces by direct union of the elements. The processes for utilizing these tendencies to union, feeble as they are, for manufacturing purposes, will be described under the compounds themselves.

THE ATMOSPHERE.

302. The components of the air may be conveniently divided into *regular* components and *accidental* components. The regular components, again, consist of three which are present in practically the same proportions in all samples, and three (namely water, carbon dioxide and dust) which vary markedly in quantity.

303. Components Present in Constant Proportions. The compounds whose proportions are practically invariable are nitrogen, oxygen and the group of inert gases. When the variable components are removed, the proportions of the constant ones are as follows:

	By volume.	By weight.
Nitrogen..............	78.06	75.5
Oxygen................	21.00	23.2
Argon.................	0.94	1.3

The inert gases, excepting argon, are present in traces only.

304. The Water Vapor. The proportion of water vapor in the air is exceedingly *variable.* When air becomes cool, the moisture *separates* in **cloud and fog,** which are composed of minute drops of liquid water. When much moisture is condensed, the drops are larger and fall as **rain.** When they fall through a cold region, they freeze to **hail.** When condensation takes place in air already below 0°, the fog is composed of solid, and not of liquid, particles. The hexagonal crystalline structures of ice which are deposited form **snow.**

On the other hand, when the weather becomes warm, evaporation goes on rapidly, especially in the neighborhood of seas, lakes, or moist country, and the proportion of water vapor in the air may be considerably *increased.*

305. Humidity. The moisture is usually defined in terms of **relative humidity,** the standard being the quantity required to *saturate* the air at the existing temperature. A space filled with air can take up aqueous vapor only until the partial pressure of water vapor becomes equal to the vapor pressure of water (p. 51) at the same temperature. The humidity is then said to be 100 per cent. If the partial pressure actually reached is only half as great as the vapor pressure of water at the same temperature, the humidity is 50 per cent. The average humidity may be placed very roughly at about 66 per cent.

At 18° (64.4° F.), the vapor pressure of water is 15.4 mm. (Appendix IV). If the total pressure of the atmosphere were 760 mm., then the air would be saturated with moisture at 18°, and have a humidity of 100 per cent, when $\frac{15.4}{760}$ or about 2 per cent of it by volume was water vapor. Upon cooling to 0°, at which temperature the vapor pressure of water is 4.6 mm., this air would retain only $\frac{4.6}{760}$, or about 0.6 per cent of moisture. At 18° there would be 15.3 grams of water in a cubic meter of air and at 0° only 4.9 grams. The difference, 10.4 grams (10.4 c.c.), would be precipitated as fog or rain from each cubic meter.

306. Test for Moisture in Air. The presence of moisture in air may be shown by placing any deliquescent (p. 90) salt, such as calcium chloride, in an open vessel. The quantity can be measured by driving a known volume of air slowly through a weighed tube containing dry calcium chloride. It may be ascertained also by noting the temperature to which the air has to be cooled before it becomes saturated and deposits fog or dew. For example, if air at 18° has to be cooled to 11° before it deposits dew, it contains water vapor at a pressure of 9.8 mm. If saturated at 18°, it would have shown 15.4 mm. Aq. Its relative humidity was therefore 9.8/15.4, or 63.6 per cent.

307. Moisture and Comfort. The chemical changes occurring in our bodies, and particularly the oxidation of waste and of digested food by the oxygen carried by the blood, are accompanied by liberation of heat. Yet our bodies must remain at 98.8° F. (37° C.). A rise of a few tenths of a degree (F.) produces noticeable discomfort. Much of the heat is lost by radiation from the surface. The extent of this loss depends upon the surface, which is invariable, and upon the surrounding temperature, which we can not always control. Non-conducting clothes reduce the radiation, and are increased in thickness in cold weather. The real adjustment, however, is accomplished, independently of radiation, by evaporation of water at the surface of the skin. The evaporation of 1 gram of water requires about 540 calories of heat. Evaporation of a single half ounce (14⅙ g.) of water will therefore lower the temperature of 76½ kilograms (168 pounds) of water (or of flesh, which is largely water) by one-tenth of a degree C. (nearly 0.2° F.).

Our comfort, then, depends upon the possibility of continual, moderate evaporation from the surface of our bodies. "Much" moisture in the air means, to us, not necessarily a great absolute amount, but a near approach to the maximum possible at the existing temperature. So the ratio of the amount present to the maximum — the humidity — is the significant fact for a practical purpose, such as feeling comfortable (or drying the wash quickly).

308. Ventilation. In winter, cold, and therefore rather dry air is brought into our rooms. When this air has been heated, its relative humidity is too low, discomfort is felt because there is too much evaporation, and moisture has to be added artificially. Here the moisture afforded by evaporation from our bodies has little effect on the air. In summer, however, the outside air is often already nearly saturated at the temperature of the room. At such times the speed of displacement by the ventilating appliances may not be great enough to keep the relative humidity down, and discomfort will arise from the opposite cause. To relieve it, the evaporation may be promoted by electric fans. They do not remove or add any air, but they stir it, and blow away the moist, nearly saturated, layers next to the skin (see § 310).

The chief purposes of **ventilation** are, therefore, to supply fresh air, to keep it in motion, and to maintain a humidity that is neither too low nor too high. Most authorities believe that, for crowded rooms, the fresh air should be continuously brought in from the outside.

309. The Carbon Dioxide. The breathing of animals, the combustion of coal and wood, and the decay (oxidation) of vegetable and animal matter produce carbon dioxide. The same gas issues from volcanoes, and often in great quantities from the soil in regions which are no longer volcanic. The proportion in the air is therefore greatest in cities and in some volcanic regions, and least in the country and over the sea. It varies from 4 parts in 10,000 in the country, to 1 per cent in crowded rooms.

Its presence may be proved in any air, and very quickly in the breath itself, by bubbling the air through calcium hydroxide solution (lime-water). Calcium carbonate is precipitated (p. 161).

310. Carbon Dioxide and Respiration. We draw about half a liter of air into our lungs at each breath, or half a cubic meter per hour. In the lungs some of the oxygen is removed, and some carbon dioxide is added.

	Fresh air, per cent.	Expired air, per cent.
Oxygen................	21.00	15.9
Carbon dioxide........	0.04	3.7

A candle flame goes out when the proportion of oxygen has fallen to 18.5 per cent. But air will sustain life until the proportion has fallen to about 10 per cent.

Nearly all experts are now convinced that the unhealthiness of over-crowded, " stuffy " rooms is not due to the increase in the proportion of carbon dioxide, which is seldom great enough to do any damage.

311. Dust in the Air. A beam of sunlight crossing a dark room can be seen by the light reflected from the particles of dust which all air contains. These are chiefly solid bodies, and are composed of salts, limestone, clay, and other rock materials, of soot and other particles of unburnt fuel, of bits of hay or straw, and of fragments of insects and other débris of plants and animals. They also include living particles, such as bacteria, and spores of plants such as moulds. The latter, when they settle upon food, germinate and give rise to putrefaction. Some of the bacteria also produce disease, when they enter the body at a place where the skin has been damaged by a cut or burn.

It is instructive to note that natural soil contains about 100,000 micro-organisms, and good, unfiltered river water from 6000 to 20,000, in each cubic centimeter. Ordinary, pure air contains only 4 to 5 micro-organisms per liter. Most of these bacteria come from the drying of soil and the dispersion of the resulting dust.

If dust were not present, we should soon notice its absence. There would be no clouds or rain. It appears that moisture will *not* condense to fog or rain in air which has been *filtered*, by being drawn through a wide tube containing a long (20 inches or more) plug of cotton, and has so been freed from dust. The particles act as nuclei, round which the liquid grows at the expense of the vapor. In the absence of dust the condensation would occur directly upon the surfaces of plants, houses, and animals. Thus, in a dustless atmosphere, an open shed or shelter, or an umbrella, would afford no protection whatever against a wetting.

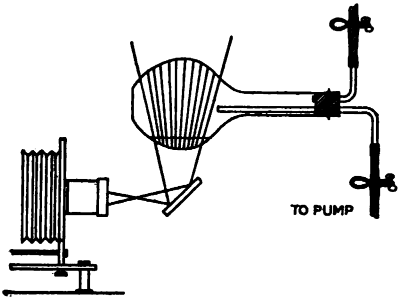

Fig. 58.

The formation of fog from ordinary air, and its non-formation in filtered air are easily shown in a darkened room (Fig. 58). The flask contains water to saturate the air. When the tube leading to the water pump is opened for an instant, the saturated air in the flask expands and is cooled. In such circumstances, ordinary air gives a fog, brilliantly illuminated by the beam of light, while filtered air (dustless) gives none.

312. Air a Mixture. The air does not contain in combined condition the various substances we have named. Each of the substances in air shows precisely the same properties which it exhibits when free, separate, and pure. This behavior is characteristic of a *mixture.*

Thus, the observed *density* of the air is precisely that which we find by calculation from the known proportions and several densities of the components. The *solubility* of each gas is observed to be the same as if it were alone present.

Again, when *liquefied air* is allowed to *evaporate* in a suitable apparatus, the nitrogen, being more volatile, can be separated *completely* from the oxygen. When the oxygen is, in turn, allowed to evaporate, the carbon dioxide and water remain as solids, frozen by the low temperature.

Finally, the *exact proportions can not be represented by a chemical formula.* This shows that the law that, in chemical compounds, the proportions can be represented by multiples of the atomic weights by whole numbers (p. 64), does not apply to air. This is a sure proof that it is not a chemical compound.

In spite of the fact that air is a mixture, the composition of the air is remarkably uniform and constant. The uniformity is due to constant mixing by the winds. The steadiness of the composition from year to year is due to the fact that, although decay and combustion continually remove oxygen and add carbon dioxide, vegetation as continually consumes the latter and restores the former (p. 165). The mass of carbon dioxide in the whole atmosphere of the planet, about 2450 thousand million tons, is so great that the amounts added and removed by the agencies just mentioned are small by comparison.

THE INERT GASES.

313. Argon. It had been shown by Lord Rayleigh that a liter of *pure* nitrogen weighed 1.2505 g., while a liter of atmospheric "nitrogen" weighed 1.2572 g. The natural inference was that the latter contained a little of some heavier gas. In 1894 Ramsay, in consultation with Rayleigh, attempted to separate this gas by passing the "nitrogen" repeatedly over heated magnesium, and so removing the real nitrogen as solid magnesium nitride Mg_3N_2. The remaining gas, about 1 per cent of the whole, was named **argon** (Greek, *lazy* or *inactive*), because it would combine with no other element.

Argon has a *molecular weight* of 39.9 (nitrogen only 28), and when liquefied *boils* at −186° and *freezes* at −189.5°.

314. Helium. An indifferent gas, previously known to be given off when uranium ores were heated in a vacuum, was found by Ramsay (1895) to be neither nitrogen, nor yet argon. By its spectrum it was recognized to be **helium** (Greek, *the sun*), a substance shown in 1868 to be present in the sun. Its *molecular weight* is 4, so that it is only twice as dense as hydrogen. It was the last gas to be liquefied (by Onnes), and the liquid *boils* at −268.7° (4.3° Abs.). Like argon, it does not enter into chemical combination.

315. Other Inert Gases. When liquefied argon was allowed to evaporate, the first vapor coming off was found to contain another gas, **neon** (Greek, *new*. Mol. wt. 20), along with helium. Careful distillation of the remaining liquid gave two other gases **krypton** (Greek, *hidden*. Mol. wt. 83) and **xenon** (Greek, *stranger*. Mol. wt. 130). The total amount of these four gases, however, was only 1 part in 80, the remaining 79 parts being pure argon. None of these gases form any compounds.

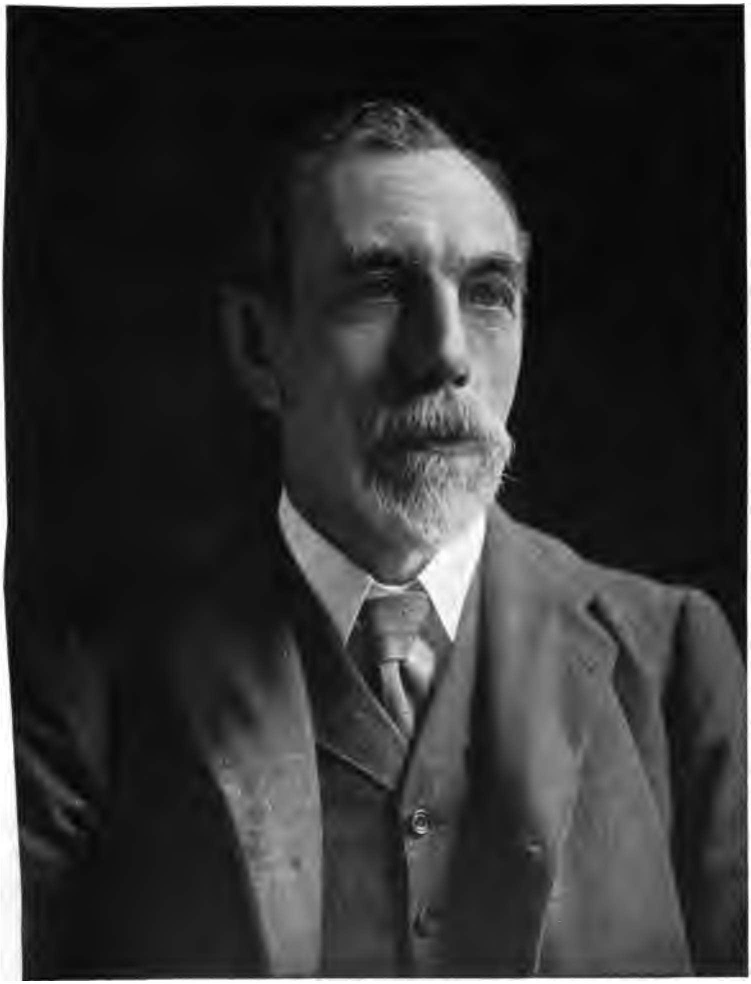

Photo by Lafayette.

SIR WILLIAM RAMSAY
Scots chemist. Discoverer of the inert elements, 1852-

Another gas, given off in minute quantities by compounds of radium, and originally known as the "radium emanation," is now found by Ramsay to be a member of this interesting group of elements, and has been named **niton** (mol. wt. 222.4). This gas is also indifferent. But it has the startling property of "disintegrating" of its own accord. It disintegrates into electricity, helium, and elements of somewhat lower atomic weight (see radium).

316. Exercises.

1. Classify (p. 100) each of the reactions represented by equations in this chapter.

2. What are the radicals of sodium nitrite, and what their valences?

3. At 77° F. the air of a room contains water vapor at a partial pressure of 20 mm. What is the percentage of humidity?

4. What weight of water is contained in a cubic meter (1000 liters) of air saturated at 10° C.?

5. What weight of carbon is contained in the total carbon dioxide in the earth's atmosphere?

6. Air at 18° has to be cooled to 14° before it deposits dew or fog. What is the percentage humidity at 18°?

7. Why is the air nearest the ground heated (by the sun) to a higher temperature than the upper air?

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XXI

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CHAPTER XXI.

AMMONIA.

317. The interest in ammonia centers largely in the use of liquefied ammonia for refrigeration, in the employment of the gas in making carbonate of soda, and in the value of its compounds as fertilizers.

318. Manufacture. Ammonia is formed when nitrogenous organic matter is heated, in absence of air. It was formerly made by distilling scraps of hoofs, horns, and hides. The solution of the gas thus obtained was called "spirit of hartshorn." The pungent odor of smoldering feathers, leather, or fur is, therefore, partly due to its presence in the escaping vapors. From the proteins of the original plants, coal derives a considerable proportion of nitrogenous matter. Hence, when coal is distilled for the making of coal gas, or, on a far larger scale, for the making of coke, much ammonia can be separated, by washing with water, from the mixture of gases produced. The aqueous solution is separated from the tar, neutralized with sulphuric acid, and evaporated to give the salt, ammonium sulphate $(NH_4)_2SO_4$.

$$NH_3 + H_2O \rightarrow NH_4OH \text{ (ammonium hydroxide).}$$
$$2NH_4OH + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2H_2O.$$

319. Ammonia from Coal and Shale. While most of the coke in Germany (80 per cent in 1910) is made in "by-product" coke ovens (§§ 577–579), in which the ammonia and innumerable other by-products are collected and utilized, in the United States 83 per cent of the coke is made in "beehive" ovens, in which all the vapors are burned, uselessly, on the spot. Yet ammonium sulphate is being used as a fertilizer in rapidly increasing amounts and finds a good market. In 1911 half the 135,000 tons used in this way (U.S.) were imported, paying duty, while ammonia capable of yielding 400,000 tons of ammonium sulphate worth $24,000,000 were wasted by the coke-makers.

The distillation of coal is the chief source of commercial ammonia. In Scotland, however, oil-bearing shale is distilled for the purpose of extracting the petroleum, and much ammonia, liberated at the same time, is collected. Formerly it was allowed to escape, but, in the absence of a protective tariff, the competition of petroleum from American and Russian wells compelled economy. Now, the profit on the ammonium sulphate pays the whole cost of mining and distilling the shale.

320. Synthetic Ammonia. The latest method of manufacturing ammonia is by the direct union of hydrogen and nitrogen. As ammonia gas decomposes almost completely when heated at 700°, it must be made below this temperature. The union of the gases is exceedingly slow. But, below 500°, in presence of a contact agent — such as specially prepared iron or uranium (Haber's process) — the gases, delivered at 185 to 200 atmospheres pressure, unite to give about 8 per cent of the compound each time they are led over the metal. The product is dissolved out with water. The required hydrogen is obtained by the action of steam on iron (p. 39), or as a by-product from the making of chlorine and sodium hydroxide (p. 107). The nitrogen is obtained by passing air over heated iron, or from liquid air (§ 312).

321. Preparation in the Laboratory. In the laboratory ammonia is most readily made by heating a mixture of a salt of ammonium, such as the chloride (NH_4Cl) or sulphate, and slaked lime $Ca(OH)_2$.

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_4OH \rightarrow 2NH_3 + 2H_2O.$$

The ammonium hydroxide, formed by the double decomposition, immediately decomposes. To free the gas from water vapor, it is passed through a tower filled with quicklime CaO (Fig. 59):

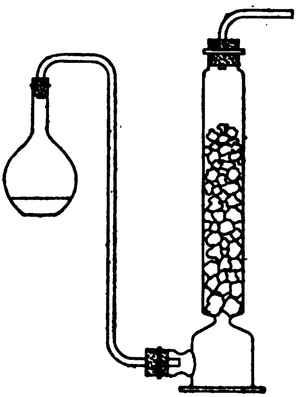

Fig. 59

$$CaO + H_2O \rightarrow Ca(OH)_2.$$

Sometimes, a stream of the gas is generated by warming commercial ammonium hydroxide solution (*aqua ammonia*), and drying the gas as above. Liquefied ammonia is obtainable in small iron cylinders, and is a convenient source when much of the gas is required.

The liberation by hydrolysis of nitrides, already noted (p. 191), is interesting:

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3.$$

322. Composition of Ammonia. That ammonia contains nitrogen may be shown by passing the gas over cupric oxide heated in a tube, and collecting the nitrogen over water:

$$2NH_3 + 3CuO \rightarrow 3Cu + 3H_2O + N_2.$$

The hydrogen may be liberated by drying the ammonia, if necessary, with soda-lime, and leading it through a tube containing heated magnesium ribbon:

$$2NH_3 + 3Mg \rightarrow Mg_3N_2 + 3H_2.$$

323. Physical Properties. Ammonia is a *colorless* gas. It has a soapy *taste*, and a very pungent *odor*. Its *density*, recorded in the formula NH_3, indicates that it is only about half as heavy, bulk for bulk, as air (14 + 3 = 17, against 28.95). It is easily *liquefied*, boiling at −38.5°, and exert-ing a pressure of 6 atmospheres at 10°. The gas is exceedingly *soluble* in water (1 vol. Aq : 1300 vol. of NH_3 at 0°). A 35 per cent solution is sold as "concentrated ammonia."

The extreme solubility in water may be shown by the "fountain" experiment (Fig. 60). The flask is filled by downward displacement of air. The long tube is closed by a short rubber tube and a clip at the bottom (not shown). The "dropper" contains water, and is closed at the tip with soft wax. The drop of water, expelled by pinching the "dropper," dissolves at once so much of the gas that the water rushes in, like a fountain, through the longer tube.

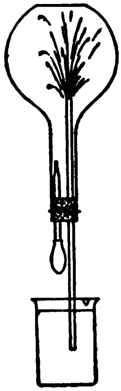

Fig. 60

324. The Solubility of Gases. It will aid us in recalling the solubilities of the various gases in water if we summarize the facts about those thus far described. The gases may be divided into three groups:

1. **Slightly soluble:** Oxygen, hydrogen, methane, nitrogen, the inert gases.
2. **Moderately soluble:** Chlorine, carbon dioxide.
3. **Very soluble:** Hydrogen chloride, ammonia, sulphur dioxide.

The gases of the first group are, in a general way, about ten times as soluble in other liquids (oils, etc.) as in water.

325. Chemical Properties. Ammonia, as we have seen, is *not very stable*, and decomposes rapidly and almost completely above 700°. A discharge of sparks from an induction coil has the same effect more gradually, and so a sample of the gas confined over mercury in a closed tube may be shown to double in volume when decomposed. Every two molecules give four:

$$2NH_3 \rightarrow 3H_2 + N_2.$$

The most characteristic property of ammonia is that it *combines directly with acids*, giving ammonium salts:

$$NH_3\,(\text{gas}) + HCl\,(\text{gas}) \rightarrow NH_4Cl\,(\text{solid particles}).$$
$$2NH_3 + H_2SO_4\,(\text{liq.}) \rightarrow (NH_4)_2SO_4\,(\text{solid mass}).$$

It *combines also with water* at a very low temperature (−98°) to give ammonium hydroxide, a white solid:

$$NH_3 + H_2O \rightleftarrows NH_4OH.$$

As the solid dissociates above −79°, a solution of the substance, made by dissolving the gas in a great excess of water, is the only form of ammonium hydroxide convenient for use.

326. Ammonium Hydroxide. This substance, as indicated by the way in which we have written its formula, is a *base*. The ions are $(OH)^-$, given by all bases, and $(NH_4)^+$, ammon*ium*-ion, which is found also in the salts mentioned above. The latter is a compound positive radical, playing the part of a metallic element.

As a base, ammonium hydroxide, although rather weak (little ionized), turns red litmus blue, possesses the characteristic soapy taste and feeling, and enters into double decomposition with acids, neutralizing (p. 129) them:

$$NH_4OH + HCl \rightarrow H_2O + NH_4Cl.$$

The salts, obtained by evaporation, are, of course, identical with those formed by union of ammonia with the same acids.

Ammonium hydroxide used to be known as "volatile alkali," in deference to the fact that it decomposes into its constituents ($NH_3 + H_2O$), both of which are volatile, while the other alkalies (NaOH, etc.) are not volatile ("fixed"). This property was utilized in the laboratory method of making ammonia (p. 201).

327. The Salts of Ammonium. The salts are ionized in aqueous solution, giving NH_4 as the positive ion:

$$(NH_4)_2SO_4 \rightleftarrows 2NH_4^+ + SO_4^=$$

When *heated*, dry, in a tube, they are decomposed. Most of them give ammonia and an acid:

$$NH_4Cl \rightleftarrows NH_3 \uparrow + HCl \uparrow$$
$$(NH_4)_2SO_4 \rightleftarrows 2NH_3 \uparrow H_2SO_4 \uparrow$$

If the acid is also volatile at, or below, a red heat, like sulphuric acid H_2SO_4, *the whole salt usually vaporizes.* These actions are reversible (read the equation backwards). Hence the acid and the ammonia recombine, and the salt condenses again in a cold part of the tube. This behavior helps us to recognize a salt of ammonium, for the salts of mercury are the only others which behave in this way.

328. Uses of Ammonia. Some of the uses have already been mentioned. The ammonia process for making carbonate of soda is described under the latter substance. The making of ammonium sulphate from ammonia is sufficiently explained in the preceding sections, and the value of the salt as a fertilizer has been mentioned (§ 319, see also § 572).

Refrigeration by liquid ammonia depends upon the fact that liquid ammonia, like any other liquid, absorbs heat in evaporating. It absorbs 330 cal. per gram. To freeze one gram of water at 0°, 80 calories have to be subtracted. Thus, 1 gram of liquid ammonia, in evaporating, will convert about 4 grams of water to ice. The same principle is also largely used for cooling air (in storage rooms for meat, etc.).

The machinery is represented diagrammatically in Fig. 61. The ammonia, first admitted from a bomb of liquefied ammonia, is driven by the pump *F* along the tube *E* and condenses to liquid form in the tube coiled in the tank *AB*.

Cold water circulates through *AB*, and removes the heat produced by the compression and liquefaction of the gas. The liquid ammonia is allowed to drip through the stopcock *G* into the lower coil. This is kept exhausted by the compressor *F*, and the liquid ammonia evaporates. In doing this, it takes heat from a 30 per cent solution of calcium chloride in water, which does not freeze even at -12°. This cooled brine leaves the tank at *D*, circulates through another tank (not shown) in which the water-filled ice moulds are suspended, and returns to *C*. When used for cooling refrigerating chambers, the brine passes through a system of pipes suitably placed in the cold-room. The whole machinery is made of iron, as copper and brass are corroded by the ammonia.

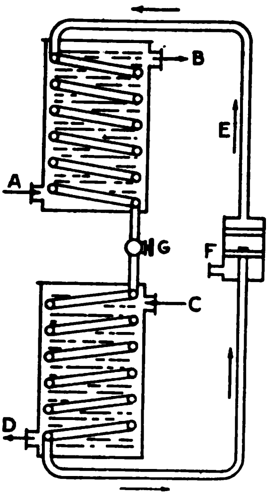

Fig. 61

Ammonium hydroxide solution is sold under the name of **household ammonia**, and is used, in washing and cleaning, to soften the water.

329. Exercises.

1. Classify the reactions shown by equations in this chapter.
2. How could you recognize the nitrogen and the hydrogen (§ 322)?
3. Why not dry ammonia gas with concentrated sulphuric acid or with phosphorus pentoxide?
4. How could you separate a mixture of oxygen and ammonia?
5. In what relative volumes do ammonia and hydrogen chloride unite?
6. Write in ionic form the equations for the interaction of ammonium hydroxide: (a) with sulphuric acid (§ 318); (b) with hydrochloric acid (§ 326).

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CHAPTER XXII.

SULPHUR AND HYDROGEN SULPHIDE.

330. Sulphur, the compounds of which have been so often mentioned, provides us, in sulphuric acid, with a substance which has more extensive and more important applications in commerce than any other chemical. The element sulphur, itself, enters, with potassium nitrate and charcoal, into gunpowder. Vulcanite is a compound of caoutchouc (rubber) and sulphur. Sulphur is employed to destroy fungi on grape-plants, and furnishes sulphur dioxide for bleaching and disinfecting.

331. Sources. The greater part of the sulphur of commerce comes from Sicily and Louisiana. In Sicily, free sulphur is mixed with pumice and other rocks. When the lumps of rock, obtained by mining or quarrying, are heated, the sulphur melts and runs to the bottom of the kiln. This product is far from pure, and is distilled from iron retorts. The vapor is condensed in chambers of brick, and the liquid is run into moulds, giving **roll sulphur.** The first vapor condensed, while the chambers are cold, yields **flowers of sulphur.**

In Louisiana the sulphur occurs in a deposit over half a mile in diameter, below 900 feet of clay, quicksand, and rock. It is obtained by means of borings, which permit four pipes, one within the other, to reach the deposit. Water, previously heated under pressure to a temperature of 170°, is pumped down the two outside pipes (6 and 8 inches in diameter). After time has been allowed for the melting of a quantity of the sulphur (it melts at 114.5°), compressed air is pumped down through an inner, one-inch pipe. The melted sulphur, alone, has twice the specific gravity of the water in the outer pipes. But the mixture of air and sulphur has about the same specific gravity, and so flows freely up a three-inch pipe which surrounds the air pipe. The sulphur runs into wooden enclosures, measuring 150 by 250 feet, in which it quickly solidifies. The product is so pure that, for most purposes, no other treatment is required. The output, at Sulphur, Louisiana — 500 tons a day from each well and, in all, 250,000 tons annually — supplies the whole demand of the United States, and could easily be increased.

A number of sulphates, such as gypsum ($CaSO_4, 2H_2O$) and barite ($BaSO_4$), and several sulphides, such as galena (PbS), zinc blende (ZnS), and pyrite (FeS_2), are found in large quantities as minerals. The last two sulphides are used in the manufacture of sulphuric acid.

332. Allotropic Forms of Sulphur. Sulphur appears in two different liquid forms, and in two familiar and perfectly distinct solid varieties. The two latter are called, from their crystalline forms, **rhombic and monoclinic** sulphur.

333. Physical Properties of Rhombic Sulphur. This form is *yellow*, with *specific gravity* 2.06. Natural sulphur, roll sulphur, and practically all of most specimens of flowers of sulphur are of this variety, and are identical in all physical properties. Specimens of natural sulphur often show the rhombic crystalline form very clearly. All the forms of sulphur are *insoluble* in water, and all the crystalline forms are *soluble* in carbon disulphide. Good rhombic crystals are obtained from the solution (Fig. 8, p. 13).

The rhombic form is stable when not heated above 96°. If kept above this temperature, it slowly changes into monoclinic sulphur.

334. Monoclinic Sulphur. This form is obtained most quickly by first melting some sulphur (m.-p. 114.5°), and then allowing it slowly to cool. As the temperature is now above 96°, the crystals which grow in the liquid are of the monoclinic variety. They are long, transparent, pale-yellow needles (Fig. 62), almost rectangular in section, and bevelled at the points. A brown tint is due to impurities. The specific gravity is 1.96. This form can be kept indefinitely above 96°, but, when allowed to cool below that temperature, it slowly becomes opaque, changing into particles of rhombic sulphur. Heat is given out during this change, as it always is in the passage from any state to one stable at a lower temperature.

Fig. 62

335. The Two Liquid Forms: Amorphous Sulphur. When sulphur is melted, and the liquid is heated, two fluid, mutually soluble forms of sulphur are produced. These are known as S_λ and S_μ or amorphous sulphur. As the temperature rises, the second variety increases in quantity (with absorption of heat) at the expense of the first variety. When the temperature is lowered, the reverse change occurs:

$$S_\lambda \rightleftarrows S_\mu \text{ (amorphous).}$$

If the temperature is lowered slowly, therefore, only monoclinic sulphur (by crystallization of the S_λ) is obtained. But if the liquid is quickly chilled, by pouring into a cold vessel or into cold water, the S_μ is found as a non-crystalline substance mixed with the crystalline form. The crystalline form can be dissolved out with carbon disulphide, leaving the **amorphous sulphur** (Greek, *without form*) which is not soluble. The proportion of S_μ varies from 3.6 per cent at 120°, to 11 per cent at 160° and about 30 per cent at 445° (the boiling-point of sulphur). S_μ is very viscous, so that, as its quantity increases, the whole mixture becomes thick. Much of the brown color, however, is due to impurities.

Amorphous sulphur is held to be a *super-cooled liquid*, and not a true solid, for true solids are all crystalline. At room temperature it changes into rhombic sulphur, but so slowly that the transformation even of a small part of it can be detected (by treating with carbon disulphide) only after the lapse of many months. At 100° the change is complete in less than an hour.

Elastic sulphur. When the melted sulphur is chilled, the amorphous sulphur does not at once become hard. When the sulphur has been heated to a high temperature, therefore, the chilled material consists at first of a sticky, transparent, elastic material, called **elastic** or **plastic sulphur.** In the course of forty-eight hours, however, this becomes opaque and hard, because of the separation of the crystalline and the hardening of the amorphous varieties.

336. Melting- and Freezing-Points. Amorphous sulphur, like glass and other amorphous substances, softens when heated, but has no sharp melting temperature. The two crystalline forms have different melting-points, rhombic at 112.8° and monoclinic at 119.25°. But these are difficult to observe, as the rhombic begins to turn into monoclinic above 96°, and both tend to give amorphous sulphur. The latter lowers the freezing-point of the liquid and the melting-points of both solids. Hence, the only temperature which is easy to observe is that at which both the solid forms melt when heated *very slowly*, and that at which the liquid freezes if cooled very slowly, namely 114.5°. This is the so-called *natural freezing-point* of sulphur.

337. Chemical Properties. The vapor density of sulphur indicates that the vapor is a mixture of the molecules S_8, S_6, and S_2, the former diminishing and the latter increasing in number as the temperature is raised.

All the *metals*, excepting gold and platinum, *combine* with sulphur to form sulphides, and in most cases much heat is given out during the union. Sulphur unites with *chlorine* to give sulphur monochloride S_2Cl_2, used in vulcanizing rubber, and burns in *oxygen* to give sulphur dioxide:[*]

$$S + O_2 \rightarrow SO_2.$$

In these compounds the *valence* of an atomic weight of sulphur appears to be one (in S_2Cl_2) or four (in SO_2). These are exceptional values, however, the common valences being two (in H_2S, ZnS, etc.) and six (in SO_3, SO_2Cl_2, etc.).

Moist sulphur is slowly *oxidized* at ordinary temperatures to sulphuric acid:

Skeleton: $S + H_2O + O_2 \rightarrow H_2SO_4.$
Balanced: $2S + 2H_2O + 3O_2 \rightarrow 2H_2SO_4.$

In the equations, the simple formula S is used in place of a molecular formula. The latter is needed only when questions about the volume of the vapor are asked, and sulphur is almost always used only in solid or melted form. Then too, the vapor contains several kinds of molecules, and using S_8 or S_6 would introduce large and inconvenient coefficients.

HYDROGEN SULPHIDE H_2S.

338. Occurrence. Sulphur is a constituent of albumen, of which, for example, the white of an egg is composed. When decay takes place within the shell, so that air is excluded and the oxidation which accompanies ordinary decay is prevented, the sulphur gives hydrogen sulphide. The latter can be recognized by its odor. Some mineral waters contain a small amount in solution.

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[*] Traces of sulphur trioxide are formed at the same time. They give minute drops of sulphuric acid, which cause a haziness in the gas when it is formed by this action.

339. Preparation. Hydrogen and sulphur combine so slowly that at 310° the completion of the union requires seven days. A *trace* may be obtained in a few minutes by leading hydrogen over sulphur, melted in a bulb (Fig. 63). A strip of paper, dipped in lead acetate solution and placed in the wide part of the tube, is darkened by the formation of lead sulphide PbS (black), while acetic acid is also formed:

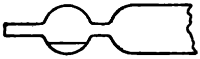

Fig. 63

$$Pb(CO_2CH_3)_2 + H_2S \rightarrow PbS + 2HCO_2CH_3.$$

Laboratory Method. The gas is commonly made by double decomposition, using a sulphide to get the S radical, and an acid for the H radical. Ferrous sulphide, made by heating iron filings and sulphur, is the cheapest sulphide, and it interacts easily with hydrochloric acid or sulphuric acid:

$$FeS + 2HCl \rightleftarrows FeCl_2 + H_2S \uparrow$$

The action, like all double decompositions, is reversible. But use of an excess of hydrochloric acid forces it forward, and the escape of the gaseous hydrogen sulphide reduces the backward action almost to zero. The gas can be made in a flask fitted like that in Fig. 16 (p. 40), or in a Kipp's automatic generator (Fig. 64). It can be collected by upward displacement.

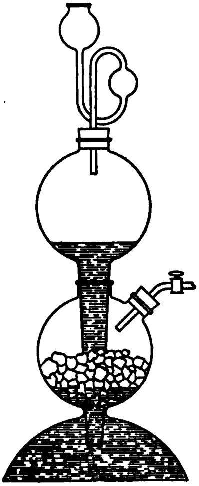

Fig. 64

340. Valence in Double Decomposition. It will be recalled that the atom of iron may be either bivalent or trivalent. In FeS it is bivalent, and it will be noted in the foregoing equation that it becomes ferrous chloride $FeCl_2$, in which it is still bivalent. It is a general rule that, *in a simple double decomposition, each element and radical carries the same valence through the action.*

341. Physical Properties. Hydrogen sulphide is a *colorless* gas with an *odor* recalling rotten eggs. It is rather easily *liquefied,* and the liquid boils at about −60° and freezes at −83°. The density, implied in the formula H_2S, shows that 22.4 liters weigh 32 + 2 or 34 g., so that the density is only one-sixth greater than that of air (of which 22.4 l. weigh 28.95 g.). The gas is moderately *soluble* in water (360 vols. in 100 vols. Aq), a property which enables us to carry out many reactions of the gas upon substances in solution.

342. Physiological Properties. Care must be taken to allow as little of the gas as possible to escape into the air, and all work with it should be done in a well-ventilated hood. The proportion must reach 1 part in 200 of air, however, before fatal results follow breathing the mixture.

343. Chemical Properties. 1. The gas *burns* in the air, giving water and sulphur dioxide:

Skeleton: $H_2S + O_2 \rightarrow H_2O + SO_2.$
Balanced: $2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2.$

2. The compound is *not very stable.* When heated, for example, in the interior of its own flame, it is decomposed into free sulphur and hydrogen. A cold porcelain dish (Fig. 65) placed in the flame will condense some of the sulphur on its surface.

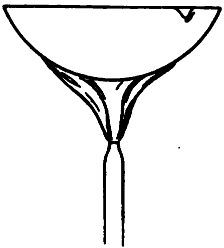

Fig. 65

3. On account of its instability, and the ease with which it gives up hydrogen, the gas is a *reducing agent.* Thus, when jars of hydrogen sulphide and sulphur dioxide are placed mouth to mouth, a deposit of sulphur gradually appears:

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S.$$

Part of the free sulphur found in nature seems to be liberated by the action of these gases, both of which are found in volcanic regions. The gases must be moist, for without water vapor as a contact agent no interaction occurs.

In this action the sulphur dioxide loses its oxygen. We say that the H_2S was *oxidized* by the SO_2, or that the SO_2 was *reduced* by the H_2S. As we have already noted, every reduction involves also an oxidation.

344. Chemical Properties — An Acid. The aqueous solution is *an acid*, and hence the compound is frequently called **hydrosulphuric acid.** It turns faintly tinted litmus paper distinctly pink. The poor conductivity of the solution shows the substance to be little ionized, and therefore a weak acid.

Like all acids, it enters into double decomposition with bases and salts. A number of these actions are used in analytical chemistry. Thus, with cupric sulphate solution we get cupric sulphide (black), and with antimony trichloride antimony trisulphide (orange), both as precipitates:

$$CuSO_4 + H_2S \rightleftarrows CuS \downarrow + H_2SO_4.$$
$$2SbCl_3 + 3H_2S \rightleftarrows Sb_2S_3 \downarrow + 6HCl.$$

If we keep in mind that the action really takes place between the ions, the first equation assumes the simpler form:

$$Cu^{++} + S^{=} \rightarrow CuS.$$

The solution surrounding the precipitate, if dilute, contains chiefly the ions H^+ and $SO_4^{=}$, along with a few molecules of H_2SO_4.

Metals displace hydrogen from the solution, but, on account of the small amount of hydrogen-ion present, the action is very slow. A striking fact, however, is the displacement of hydrogen from hydrogen sulphide by metals like silver, which do not displace hydrogen from most acids (see activity list, Appendix V). Here, the lack of activity of the silver is made up by the extreme stability and insolubility of the sulphide which is formed:

$$2Ag + H_2S \rightarrow Ag_2S + H_2.$$

Even the minute trace of silver-ion, which is all that usually would be formed:

$$2Ag + 2H^+ \rightleftarrows 2Ag^+ + H_2$$

is at once removed to give solid Ag_2S, and so the displacement is able to proceed. The tarnishing of silver in the household is due to this action, the hydrogen sulphide coming, probably, from slight leaks in the gas pipes. Illuminating gas should be free from hydrogen sulphide, but usually contains a trace of it.

345. Sulphides. As we have seen, many sulphides of metals are found as minerals. Since most sulphides are insoluble, many can be made by double decomposition. They may also be prepared by reduction of sulphates. Thus, when sodium sulphate is heated on a piece of charcoal (such as a half-burnt match) the sulphide is formed:

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO.$$

It will be observed that *in sulphides*, H_2S, Na_2S, ZnS, CuS, and so forth, *sulphur is invariably bivalent.*

346. Carbon Disulphide CS_2. This compound is an important solvent for sulphur, caoutchouc (rubber), and other substances which do not dissolve in water. It is manufactured by heating coke and sulphur together to a very high temperature. Electricity is used as the source of the heat, the resistance of the coke causing the latter to glow. The sulphur (vapor) mixed with the coke combines with the latter, and carbon disulphide passes off as vapor and is condensed. The liquid boils at 46°, and is highly inflammable:

$$CS_2 + 3O_2 \rightarrow 2SO_2 + CO_2.$$

Carbon disulphide is used as a solvent. Large quantities are employed also in the destruction of prairie dogs and for freeing grain elevators of rats and mice.

347. Exercises.

1. Write equations for the union of aluminium and of zinc with sulphur.
2. What experiments should you use to recognize a piece of sulphur?
3. In what proportions by volume do: (a) sulphur dioxide and hydrogen sulphide; (b) oxygen and hydrogen sulphide interact?
4. Make an ionic equation for the precipitation of antimony trisulphide.
5. Would equal weights of rhombic, monoclinic, and amorphous sulphur give out equal or different amounts of heat on burning? If different, which would give the most and which the least?
6. What would be the effect of passing hydrogen sulphide through a red-hot tube?

CHAPTER XXIII.

OXIDES AND OXACIDS OF SULPHUR.

348. There are two familiar oxides, namely sulphur dioxide or sulphurous anhydride SO_2, and sulphur trioxide or sulphuric anhydride SO_3. Each of these dissolves in water and combines with it to form an acid, just as does carbon dioxide (p. 161). The former gives sulphurous acid H_2O,SO_2 or H_2SO_3, and the latter sulphuric acid H_2O,SO_3 or H_2SO_4.

349. Acidic and Basic Oxides. As we have seen, an oxide, like carbon dioxide CO_2 (p. 161) or sulphur dioxide SO_2 (p. 220), which combines with water to form an acid, is said to be the *anhydride* of the acid. The *oxides of the non-metallic elements,* when they combine with water, in so doing invariably *form acids.* In the next five chapters we shall meet with other examples (*e.g.,* Cl_2O, N_2O_5, P_2O_5, SiO_2, etc.). On the other hand, the *oxides of metallic elements,* when they are able to combine with water, very frequently give *bases* (*e.g.,* $Ca(OH)_2$ from CaO, p. 202, §§ 524, 542). For convenience, therefore, we shall often speak of an oxide as an **acidic oxide** or a **basic oxide,** as the case may be.

350. Nomenclature. The acids and salts *within one group* are distinguished by the terminations of, and prefixes to, their names. Thus we have:

*Hypo*sulphur*ous* acid $H_2S_2O_4$.	Sodium *hypo*sulph*ite* $Na_2S_2O_4$.
Sulphur*ous* acid H_2SO_3.	Sodium sulph*ite* Na_2SO_3.
Sulphur*ic* acid H_2SO_4.	Sodium sulph*ate* Na_2SO_4.
*Per*sulphur*ic* acid $H_2S_2O_8$.	Sodium *per*sulph*ate* $Na_2S_2O_8$.

The proportion of oxygen to the other elements is at the basis of the system. The terminations *ous* and *ite* indicate less oxygen than *ic* and *ate*. The prefix *hypo* (Greek, *below*) implies still less oxygen. The *per*-acid contains the most oxygen.

Knowledge of one group, however, does not enable us to attach names to given formulæ from another group. Thus, $HClO_2$ and $HClO_3$ are chlor*ous* and chlor*ic* acids, and $HClO$ and $HClO_4$ the *hypo*- and *per*- acids, respectively.

The names of compounds containing only two elements (the binary compounds) end in *ide:* Zinc sulph*ide* ZnS, magnesium nitr*ide* Mg_3N_2, calcium carb*ide* CaC_2, sodium chlor*ide* NaCl, and the ox*ides* CaO, etc.

SULPHUR DIOXIDE AND SULPHUROUS ACID.

351. Preparation of Sulphur Dioxide SO_2. In *commercial practice* sulphur dioxide *is obtained* in three ways:

1.. By burning sulphur. The product is used for all purposes to which sulphur dioxide is put.

2. By burning natural sulphides, such as pyrite:

Skeleton: $FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$.

Balanced: $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$.

With fairly pure pyrite the combustion has only to be started. But with some sulphides, like zinc blende ZnS, which is used as a source of sulphur dioxide as well as of zinc, the air must be strongly heated to maintain the combustion:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2.$$

Forced combustion of an ore, like this, is called **roasting,** or **calcining,** and is the first stage towards obtaining the metal. The oxide is subsequently reduced by heating with coke.

The sulphur dioxide obtained in the process of roasting ores is not always used for any purpose, but, when used, it is made into sulphuric acid. One reason for this is that it is too much diluted to be conveniently employed for other purposes. The amount of admixed nitrogen (from the air) alone is enormous. Thus, in the case of zinc sulphide (see equation, above), $3O_2$ give $2SO_2$, or 3 volumes of oxygen give 2 volumes of the oxide. But each volume of oxygen is accompanied by four volumes of nitrogen, so that, in the end, the 2 volumes of the dioxide are mixed with at least 12 volumes of nitrogen. In practice the dilution is much greater than this.

3. By dropping concentrated sulphuric acid into red-hot iron retorts: $2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + O_2$.

Sulphur dioxide made in this way is employed for bleaching, and for the preparation of sulphites (used in paper-making).

4. *In the laboratory* a steady stream of the gas is easily obtained by dropping hydrochloric acid upon crystals of sodium-hydrogen sulphite (Fig. 38, p. 108):

$$NaHSO_3 + HCl \rightarrow NaCl + H_2SO_3 \qquad (1)$$

$$H_2SO_3 \rightleftarrows H_2O + SO_2 \uparrow \qquad (2)$$

This method takes advantage of the fact that sulphurous acid, like all acids, can be made by double decomposition (equation 1), and that this acid is unstable and decomposes (equation 2) when there is not a large excess of water present.

5. Another *laboratory method* consists in using method number 3, but adding to the sulphuric acid some substance that will aid the action (and reduce the heating required) by taking up the oxygen. Copper, charcoal, and even sulphur itself, are suitable substances.

352. Partial Equations. The equation for the foregoing action may conveniently be made by writing two preliminary or **partial** equations, and adding them together:

$$\begin{array}{rcl} H_2SO_4 & \rightarrow & H_2O + SO_2 + (O) \\ (O) + H_2SO_4 + Cu & \rightarrow & H_2O + CuSO_4 \\ \hline 2H_2SO_4 + Cu & \rightarrow & 2H_2O + CuSO_4 + SO_2. \end{array}$$

The oxygen need not here be written O_2, because it is not liberated as a gas, but cancels out, being used up to oxidize the copper. The device of writing partial equations is useful when the action is complex, as where more than two substances are used or produced. This is a purely arithmetical device, and does *not* imply that the chemical change itself takes place in more than one step.

353. Physical Properties. The usual six physical properties may be noted: The gas is *colorless*, but has a characteristic *taste* and *odor*. It has a *density* considerably greater than that of air (SO_2 = 64 against 28.95). It can be *liquefied* below 165° (the crit. temp.) and the liquid boils at −8°. As the pressure required at 20° is only 3¼ atmospheres, the liquid can be kept in bottles like syphons, or in sealed tin cans. It is extremely *soluble* in water (about 50 vols. : 1 vol. Aq). The solution is sulphurous acid.

354. Chemical Properties. Sulphur dioxide is very *stable*. It *combines with water* giving a solution of sulphurous acid. The gas is used in *bleaching* straw, silk, and wool. The bleaching action seems largely to consist in *combination* with the coloring matter, to give a colorless compound. Hence straw hats recover the yellow color of straw by exposure to light, which slowly liberates the sulphur dioxide. It kills fungi and other organisms, but has little effect if too much diluted with air. Formaldehyde is displacing it as a disinfectant.

355. Properties of Sulphurous Acid H_2SO_3. The acid is *unstable*, and the solution smells strongly of sulphur dioxide.

Sulphurous acid, in aqueous solution, shows all the properties of *an acid* very distinctly; its solution is an electrolyte, it turns litmus red, and gives double decompositions with bases and salts.

Being rather easily convertible into sulphuric acid H_2SO_4, sulphurous acid is *a reducing agent.* Thus oxygen from the air acts slowly upon the solution:

$$2H_2SO_3 + O_2 \rightarrow 2H_2SO_4$$

and iodine is turned into hydrogen iodide:

$$H_2SO_3 + H_2O + I_2 \rightarrow H_2SO_4 + 2HI.$$

356. Sulphites and Bisulphites. Sulphites are formed by neutralization:

$$2NaOH + H_2SO_3 \rightarrow Na_2SO_3 + 2H_2O.$$

With *excess* of sulphur dioxide passed into the solutions of the bases, the acid sulphites are formed:

$$NaOH + H_2SO_3 \rightarrow NaHSO_3 + H_2O.$$
$$Ca(OH)_2 + 2H_2SO_3 \rightarrow Ca(HSO_3)_2 + 2H_2O.$$

Such acid salts are known in commerce as **bisulphites,** because, the proportion of the metal being half that in a sulphite, the proportion of the sulphite radical is, relatively, twice as great.

357. Dibasic Acids. Acids containing two atoms of hydrogen in each molecule are called **dibasic acids.** H_2CO_3 (p. 162), H_2S, H_2SO_3 and H_2SO_4 are such acids. Each molecule is able to react with two molecules of a base like sodium hydroxide, as may be seen in the first of the equations in the preceding section. When half the quantity of the base is used, an *acid salt* (p. 139) is produced, as the two other equations show. Phosphoric acid H_3PO_4 is a **tribasic** acid. Hydrochloric and nitric acids HNO_3 are **monobasic.**

358. Paper Manufacture. Paper is composed of cellulose $(C_6H_{10}O_5)_y$ and is made from a mixture of cotton or linen pulp and wood pulp — the cheapest varieties from the latter alone. The wood is cut into chips and heated ("cooked") with a solution of calcium bisulphite $Ca(HSO_3)_2$. This dissolves out the lignin, which, together with cellulose, makes up the solid part of its structure. The pulpy material is then washed, beaten with water to reduce it to minute shreds, and bleached with very dilute chlorine-water. The pure cellulose, now paper pulp, suspended in water, is spread on screens, drained, pressed, and dried. During the process other substances are usually added. Thus size (gelatine, or rosin and alum) prevents the ink from running; pulverized calcium sulphate (gypsum), clay, and other white solids ("loading") give body to the paper and make possible the subsequent production of a smooth surface by rolling ("calendering"). Ultramarine (blue) and other colored powders are added to the pulp when special tints are required.

359. Other Uses of Sulphurous Acid. To prevent the growth of fungi or other organisms, wine casks are fumigated with sulphur dioxide before being filled. Dried peaches and apples are prepared by exposing slices of the fruit in trays to sulphur dioxide. The sulphurous acid produced bleaches the fruit, keeps insects away, and prevents the formation of dark-colored substances during the subsequent drying. In the United States the law (1907) permits the use of natural coloring matters, and of seven harmless coal-tar dyes, in the preparation of preserved fruits and candy for the market.

SULPHUR TRIOXIDE AND SULPHURIC ACID.

360. Preparation of Sulphur Trioxide SO_3. After sulphur dioxide has been formed, further union of the oxide with oxygen is exceedingly slow. It is easily promoted by *contact agents*, however, of which the most active are ferric oxide Fe_2O_3 and platinum. The efficiency of the contact agent depends on the amount of surface it presents to the gases. The action may be illustrated by dipping asbestos in a solution of chloroplatinic acid and then heating the mineral in the Bunsen flame:

$$H_2PtCl_6 \rightarrow Pt + 2HCl \uparrow + 2Cl_2 \uparrow$$

The platinum is thus spread in a fine grey powder on the fibers of the asbestos. The latter is placed in a tube (Fig. 37, p. 107), where a mixture of oxygen (or air) and sulphur dioxide may be passed over the heated (400°) material.

$$2SO_2 + O_2 \rightarrow 2SO_3.$$

The sulphur trioxide issues as vapor at the other end of the tube, where its presence is recognized by the dense fumes (droplets of sulphuric acid), produced when it meets the moisture in the air. The vapor can be condensed to liquid form in a cooled flask.

This **contact process** is used in the manufacture of sulphuric acid, the vapor being led into dilute sulphuric acid, in which it is absorbed more promptly than in pure water:

$$H_2O + SO_3 \rightarrow H_2SO_4.$$

The liquid sulphur trioxide becomes solid at 15°. A trace of moisture converts it into an allotropic, solid variety. This form consists of white, silky crystals which, when heated, vaporize, but do not melt.

361. Sulphuric Acid, H_2SO_4. This acid is now largely manufactured by the *contact process* described above. This is true especially of the concentrated acid, containing little or no water, which is so much used in the making of dyes, of guncotton and other explosives, and of sodium carbonate. The less concentrated acid, used in making fertilizers ("superphosphate"), comes from the **chamber process,** which is operated in connection with the roasting of sulphide ores of zinc, copper, and other metals. In this process the same substances, sulphur dioxide and oxygen and water, are combined. But a slower catalyst, nitrogen trioxide N_2O_3, obtained from nitric acid, acts upon the dilute mixture of gases in immense chambers lined with lead.

The acid is known commercially as **oil of vitriol,** because in the fifteenth century it was made by distilling green vitriol (hydrated ferrous sulphate, $FeSO_4, 7H_2O$) with sand.

362. Physical Properties of Sulphuric Acid. The acid is a *colorless,* oily *liquid* of *sp. gr.* 1.84, which freezes to a solid at 10°. It *mixes with water* in all proportions, and much heat (*heat of solution*) is given out when it dissolves. It *boils* at 338°, but the vapor contains 34 per cent of free water and sulphur trioxide, which recombine when it cools.

363. Chemical Properties. 1. The acid is more *stable* than sulphurous acid, but decomposes largely at the boiling-point.

2. Sulphuric acid is much more active as *an acid* than is sulphurous acid, but inferior in this respect to hydrochloric HCl and nitric acids HNO_3. Like other active, soluble acids, its solution turns litmus red, gives hydrogen upon addition of active metals, and enters into double decomposition with bases and salts. Thus, insoluble sulphates are precipitated:

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + 2HCl$$

Of course, the same product, barium sulphate, would be obtained with any substance containing the radical SO_4:

$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 \downarrow + 2NaCl$$

and the action is used as **a test** for this ion. As other salts of barium are insoluble in water, the sulphate is recognized by the fact that it is too insoluble to be acted upon by dilute pure hydrochloric acid or nitric acid. The other insoluble salts of barium interact with these acids and dissolve. The addition of one of these acids is therefore part of the **test** for SO_4-ion.

On account of its high boiling-point, the double decompositions of the concentrated acid can be *used for preparing more volatile acids* (such as nitric acid):

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \uparrow \text{ (gas at room temp.).}$$
$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3 \uparrow \text{ (volatile at 86°).}$$

3. Concentrated sulphuric acid combines with water to form a stable *hydrate* H_2SO_4, H_2O. Hence it removes the elements of water from many substances containing hydrogen and oxygen, and is called a **dehydrating agent.** Thus, paper (cellulose), moistened with the concentrated acid, turns black from the liberation of carbon. Sugar ($C_{12}H_{22}O_{11}$) is decomposed even more easily:

$$C_6H_{10}O_5 \rightarrow 6C + 5H_2O.$$
$$C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O.$$

4. Finally, concentrated sulphuric acid acts as *an oxidizing agent.* Sulphur and carbon, boiled in it, are oxidized:

$$2H_2SO_4 + C \rightarrow 2SO_2 + 2H_2O + CO_2$$

and metals are converted into sulphates. The action on copper (equation § 352) may be used for preparing sulphur dioxide. It should be noted that metals do not displace hydrogen, except from the *dilute* acid, because the latter alone contains the hydrogen *ions*, which are thus discharged and liberated. The concentrated acid has usually to be heated, and then the *molecules* H_2SO_4 give part of their oxygen for oxidizing purposes, and hydrogen is not liberated.

364. Sulphates. A number of sulphates are in common use. Thus partly hydrated calcium sulphate $2CaSO_4, H_2O$ is **plaster of Paris,** hydrated magnesium sulphate $MgSO_4, 7H_2O$ is **Epsom salt,** hydrated cupric sulphate $CuSO_4, 5H_2O$ is **bluestone,** used in batteries. The first is made by heating **gypsum** $CaSO_4, 2H_2O$, a common mineral. When the plaster of Paris is moistened, it "sets," and is thus used in making "plaster casts." The setting results from the reformation of gypsum:

$$2CaSO_4, H_2O + 3H_2O \rightarrow 2CaSO_4, 2H_2O.$$

365. Uses of Sulphuric Acid. The acid has innumerable applications, some of which have already been mentioned. The dehydrating power is valuable in making nitroglycerine and guncotton (Chap. XXXII). As a cheap acid, it is used to clean iron before tinning and galvanizing. Under calcium phosphate its use in making fertilizers is explained (see § 433).

The unsaturated hydrocarbons, contained in natural petroleum, are oxidized by the air to dark-colored products. Kerosene and other oils, during their manufacture, are therefore agitated with concentrated sulphuric acid, which combines with such compounds, and leaves an oil which remains colorless when kept.

366. Exercises.

1. Which contains more oxygen: (a) a phosphate or a phosphite; (b) a nitrite or a nitrate; (c) a borate or a perborate? Name the acids corresponding to these six salts.
2. Make equations for: (a) the roasting of stannic sulphide (SnS_2) giving SnO_2; (b) the action of concentrated sulphuric acid on silver giving silver sulphate and SO_2 (use partial equations); (c) the dissociation of sulphuric acid vapor.
3. What are the formulæ of magnesium sulphite and bisulphite, respectively?
4. Give two reasons why boiling sulphuric acid, when spilt upon the flesh, causes most serious burns.
5. By what facts or tests could you recognize concentrated sulphuric acid?
6. Why is the wooden laboratory shelf commonly "burned" where the sulphuric acid bottle stands?
7. What would be the reaction between sodium sulphite and sulphuric acid?
8. How could you distinguish between, and recognize, the sulphide, sulphite, and sulphate of potassium?

CHAPTER XXIV.

OXIDIZING SUBSTANCES.

367. Nitric acid, which we shall take up in the next chapter, shows a variety of very different chemical properties. One of these is the property of oxidizing other substances. In order to understand these oxidations, and to see at once the difference between the oxidizing actions, and the other actions which the acid exhibits, we must now learn more about oxidation in general. We can do this best through the study of three oxidizing substances which are of a simpler nature and are all in common use. These are **ozone, hydrogen peroxide, and hypochlorous acid.**

OZONE O_3.

368. When oxygen is blown from a small nozzle through the tip of a Bunsen flame, a part of it is turned into ozone. The same thing happens when a platinum wire, heated by an electric current, is held under liquefied oxygen. This shows us that, to get ozone, we must add *energy* (for example, by strong heating) to oxygen. We learn, also, that the ozone must be cooled at once and kept cold. If it lingers in the cooler (but not cold) region round the flame, it decomposes again.

369. Preparation of Ozone. In practice electrical energy, developed by passing a "silent discharge" through the oxygen, is employed. This discharge gives ozone most plentifully, and most easily, because its use involves no rise in temperature whatever.

$$3O_2 \rightarrow 2O_3.$$

The poles of the induction coil are attached to the tinfoil upon the outside of the outer tube and the inside of the inner tube (Fig. 66). The "discharge" therefore passes through two layers of glass, as well as through the oxygen. The oxygen, from a cylinder of the gas, flows slowly through the space between the tubes. At best, only 6 to 7 per cent of the oxygen is usually changed into ozone.

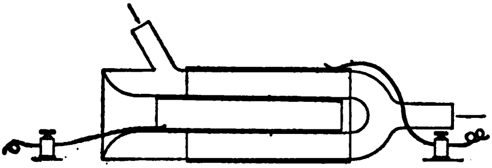

Fig. 66

370. Physical Properties. Ozone (Greek, *to smell*) is a gas of *deep blue* color, with a fresh, highly individual *odor*. It is more easily *liquefied* than is oxygen (b.-p. $-119°$), and is also much more *soluble* in water. Its *density* is one-half greater than that of oxygen, and the formula O_3 records this fact. Ozone and oxygen are, therefore, allotropic forms of the same element.

371. Chemical Properties. Ozone, being produced by giving energy to oxygen, is at rather low temperatures (*e.g.*, from 10° to 500°) the *less stable form* of the element. Upon standing, and more quickly when warmed, it changes into oxygen, with liberation of the additional energy it contains.

Being possessed of more internal energy than oxygen, ozone *oxidizes* the same substances as does oxygen, only more rapidly and vigorously. Hence, it instantly oxidizes sulphur dioxide to sulphur trioxide, and sulphurous acid to sulphuric acid:

$$SO_2 + O_3 \rightarrow SO_3 + O_2.$$
$$H_2SO_3 + O_3 \rightarrow H_2SO_4 + O_2.$$

For the same reason it oxidizes many substances not affected by ordinary oxygen. Thus, it rusts silver to black silver peroxide Ag_2O_2.

$$2Ag + 2O_3 \rightarrow Ag_2O_2 + 2O_2.$$

As a rule, only the one extra atom of oxygen in the molecule of ozone is used for the oxidation.

Ozone also *oxidizes* a number of *organic compounds* which are unchanged in atmospheric oxygen. For example, when ozonized oxygen is bubbled through a dilute "indigo" solution (*e.g.*, of indigo carmine), a yellow substance, of much paler tint, isatin, is formed, and the indigo is said to have been **bleached.** Indigo is taken, for illustration, because it is a most widely used dye, employed in dying navy-blue and blue-black goods, and is little affected by light, and by oxygen, soap, and other ordinary substances:

$$\underset{\text{indigo}}{C_{16}H_{10}N_2O_2} + 2O_3 \rightarrow \underset{\text{isatin}}{2C_8H_5NO_2} + 2O_2.$$

Litmus, and the traces of coloring matter in wax, starch, flour, and ivory are all oxidized by it to colorless, or nearly colorless, substances. For this reason it is used commercially in bleaching the last-named materials.

Ozone is sometimes recommended for use, in connection with ventilation, as a means of destroying minute organisms in the air. Recent investigations have shown, however, conclusively, that, when thus diluted with air, it is valueless as a germicide. It is employed by some cities (*e.g.*, Paris, Florence, and St. Petersburg) for sterilizing the water supply.

From the foregoing we see that, by an **oxidizing agent,** like ozone, we ordinarily mean **a substance which is a better oxidizer than free atmospheric oxygen.**

HYDROGEN PEROXIDE H_2O_2.

372. Preparation. Sodium peroxide Na_2O_2, produced by burning sodium in dry air, can be dissolved, a little at a time, in *ice-cold* water. When this solution is acidified with hydrochloric or sulphuric acid, a double decomposition takes place:

$$Na_2O_2 + 2HCl \rightarrow 2NaCl + H_2O_2$$

and a dilute solution of hydrogen peroxide (mixed with common salt) is obtained. The nature of the action shows the product to be an acid, with the negative radical O_2^{II}.

For manufacturing purposes it is more convenient to use barium peroxide BaO_2, suspended in water, and sulphuric acid:

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + H_2O_2$$

because the barium sulphate is insoluble and can be removed by filtration.

In pharmacy a 3 per cent solution is the one commonly sold. As hydrogen peroxide decomposes at 100°, the pure substance can be obtained only by reducing the pressure of the air in the closed distillation apparatus to 26 mm., and distilling off the water at 27°.

373. Properties. Hydrogen peroxide is a colorless, syrupy *liquid* of sp. gr. 1.5, *miscible* with water in all proportions. Dilute solutions have a metallic *taste*.

Chemical Properties 1. As an *acid*, hydrogen peroxide enters into double decomposition, particularly with bases, giving salts containing the radical O_2:

$$Ca(OH)_2 + H_2O_2 \rightarrow CaO_2 \downarrow + 2H_2O.$$

The salts are now often called **peroxidates,** instead of peroxides, as sodium peroxidate and barium peroxidate, and the acid itself is sometimes called hydrogen peroxidate. The latter is a very feeble acid, hardly affecting litmus.

2. When the solution is heated, the compound *decomposes*, with evolution of heat, giving water and oxygen:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \uparrow$$

Contact agents hasten the decomposition. Thus, it takes place with frothing when the cold solution is applied, as an antiseptic, to cuts or sores, or when powders, such as manganese dioxide, are thrown into the solution.

3. Since hydrogen peroxide, like ozone, gives off oxygen with liberation of energy, it is *an oxidizing agent* also. In this respect its behavior is very similar to that of ozone. Thus, it oxidizes sulphurous acid to sulphuric acid:

$$H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O.$$

It oxidizes colored organic compounds to colorless ones, and is, therefore, used in bleaching hair, feathers, silk, and ivory. It is also fatal to micro-organisms, and is, therefore, employed in medicine to disinfect wounds and as a throat wash.

In oil paintings the high lights are produced in part with white lead (carbonate of lead). These disappear and the picture darkens with age, because hydrogen sulphide in the air turns the white lead into the black, lead sulphide PbS. In picture restoring the latter is oxidized to lead sulphate, which is white, by treatment with hydrogen peroxide solution.

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O.$$

4. A beautiful reaction is used as a *test*. When potassium dichromate solution is acidified with sulphuric acid, to liberate the dichromic acid:

$$K_2Cr_2O_7 + H_2SO_4 \rightarrow H_2Cr_2O_7 + K_2SO_4$$

and a drop of the mixture containing the latter acid is added to aqueous hydrogen peroxide, a substance possessing a deep, brilliant blue color is formed. By this test the presence of hydrogen peroxide in rain water can often be demonstrated.

HYPOCHLOROUS ACID $HClO$.

374. Pure Hypochlorous Acid. A pure solution of the acid may be made by dissolving the corresponding anhydride in water. The anhydride, **chlorine monoxide Cl_2O**, is a brownish-yellow, explosive gas, made by passing chlorine gas over warmed mercuric oxide * (Fig. 57, p. 190):

$$2Cl_2 + HgO \rightarrow HgCl_2 + Cl_2O.$$
$$Cl_2O + H_2O \rightarrow 2HClO.$$

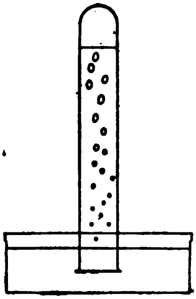
Fig. 67

As *an acid*, hypochlorous acid is very weak, being very little decomposed into its ions, H^+ and $(ClO)^-$.

It is *unstable*, exposure to sunlight being sufficient to cause it to give up oxygen, which rises in bubbles through the solution (Fig. 67):

$$2HClO \rightarrow 2HCl + O_2 \uparrow$$

Heat is given out in the action, and the stable hydrochloric acid remains.

It is a most *active oxidizing agent*, because of this tendency to give up oxygen with liberation of energy. Thus, its solution instantly oxidizes sulphurous acid to sulphuric acid:

$$H_2SO_3 + HClO \rightarrow H_2SO_4 + HCl.$$

The solution also oxidizes organic colored substances, producing colorless or less strongly colored ones:

$$\underset{\text{indigo}}{C_{16}H_{10}N_2O_2} + 2HClO \rightarrow 2\underset{\text{isatin}}{C_8H_5NO_2} + 2HCl.$$

Used as a disinfectant (see § 377), it oxidizes and destroys bacteria. Hypochlorous acid is *more energetic* as an oxidizing agent than is ozone or hydrogen peroxide.

375. Chlorine-Water. Hypochlorous acid made from chlorine monoxide is much too expensive for application in the bleaching industry. But fortunately, on account of its great

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* The mercuric oxide must be made by precipitation from sodium hydroxide and mercuric nitrate solutions, and must be well washed with water, and completely dried before use.

activity as an oxidizer, a very dilute solution is all that is required, and is, indeed, all that can safely be used. Hence, in practice, chlorine-water, which can be made very cheaply, is the form in which hypochlorous acid is always employed.

It will be recalled that chlorine acts chemically upon water (§ 170):

$$Cl_2 + H_2O \rightleftarrows HCl + HClO$$

giving hydrochloric acid and hypochlorous acid. The action is reversible (read the equation backwards), and in half-saturated chlorine solution about one-third only of the chlorine has undergone the change shown in the equation. But, if a substance which can be oxidized, such as a dye (attached, perhaps, to cloth), is introduced into the solution, the HClO which is present transfers its oxygen to the dye-stuff. This leaves HCl *alone* in the solution, and stops the backward reaction. Hence more of the chlorine acts upon the water, and more hypochlorous acid is formed. This, in turn, is used up. Thus, in a few moments, all the free chlorine is gone, only dilute hydrochloric acid remains, and a colorless organic compound is left on the cloth or in the solution. The mechanism seems complicated, but in reality is of a sort with which we are quite familiar. It is like keeping one's money in a bank, where it exists, perhaps, largely in the form of loans and bonds. We then draw it out *as it is needed*, instead of carrying it all, loose, in our pockets.

Sunlight acts upon chlorine-water, exactly as it does on any other solution of hypochlorous acid, causing oxygen to be given off. In this case, also, only hydrochloric acid finally remains:

$$2Cl_2 + 2H_2O \rightleftarrows 2HCl + 2HClO \rightarrow 2HCl + O_2 \uparrow$$

Chlorine itself is often, erroneously, spoken of as the bleaching agent. If a *dry*, colored cloth be hung for a week in chlorine, *dried* by having sulphuric acid in the bottle (Fig. 68), little or no change in color will occur. But a *wet* rag is bleached as soon as the chlorine has time to dissolve in the water, and give the necessary hypochlorous acid.

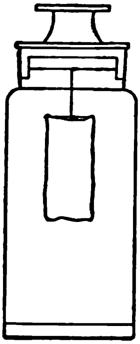
Fig. 68

376. Bleaching. Cotton and linen, in their original states, are not pure white. Bleaching is therefore an extensive and most important industry. The yarn or cloth must first be freed from cotton-wax and tannin, since the former would hinder the action of the bleaching agent, and both would also make the subsequent dyeing uneven. The material is therefore first boiled with dilute caustic soda solution, and washed with water. The cloth is then saturated with bleaching powder solution, and is piled loosely until the coloring matter has been oxidized. The goods are then washed with extreme thoroughness.

Bleaching powder $CaCl(OCl)$ is made by the action of chlorine on quicklime:

$$CaO + Cl_2 \rightarrow CaCl(OCl).$$

A strong acid, such as sulphuric acid, acts upon it by double decomposition:

$$CaCl(OCl) + H_2SO_4 \rightarrow CaSO_4 + HCl + HClO \rightleftarrows Cl_2 + H_2O.$$

A weak acid, however, like carbonic acid (see § 377), can liberate the hypochlorous acid only.

In bleaching, as a rule, no active acid is added. The effect is produced by the bleaching powder itself, supplemented by hypochlorous acid liberated by the action of carbon dioxide from the air. The final washing, to remove all traces of chlorine and bleaching powder, is absolutely necessary. If not removed, the hypochlorous acid and lime act gradually upon the cotton or linen, and "rot" it. Bleaching agents, when used in the household, carelessly, are liable to cause extensive damage from this cause.

Cotton and linen $(C_6H_{10}O_5)_y$ are rather indifferent chemical substances (p. 187), and stand *brief* contact with dilute chlorine-water without much alteration. But wool and silk contain compounds of nitrogen (proteins) and are acted upon as rapidly as are the traces of colored matter themselves. Hence sulphurous acid is used for bleaching these materials.

377. Bleaching Powder as a Disinfectant. A disinfectant is a substance which destroys bacteria and other minute, and often harmful organisms. Bleaching powder $CaCl(OCl)$ has a distinct odor of hypochlorous acid (or Cl_2O, *not* chlorine). This is due to the action of carbonic acid, derived from carbon dioxide in the air, which is able to displace the weak acid ($HClO$), but not the much stronger one (HCl):

$$2CaCl(OCl) + H_2CO_3 \rightarrow CaCl_2 + CaCO_3 + 2HClO.$$

The dry powder will *disinfect* the surrounding *air*, because of the oxidizing power of the hypochlorous acid thus liberated.

When an epidemic of typhoid fever occurs, it is usually traced to the presence of colon bacilli in the *drinking water*. The most effective means of destroying these bacilli is to add, at the distributing point, a small proportion of bleaching powder (about 20 pounds per million gallons of water). The salt is hydrolyzed (p. 181), so far as the hypochlorous acid radical is concerned, giving basic calcium chloride (§ 216), and the free acid kills the bacteria:

$$CaCl(OCl) + H_2O \rightarrow CaCl(OH) + HClO.$$

378. Oxidations Previously Mentioned. The simplest oxidations are the *unions of oxygen* with metals and with non-metals:

$$2Cu + O_2 \rightarrow 2CuO.$$
$$2C + O_2 \rightarrow 2CO.$$
$$S + O_2 \rightarrow SO_2.$$

The union of *more* oxygen with an oxide or an oxacid is oxidation also:

$$2CO + O_2 \rightarrow 2CO_2.$$
$$2SO_2 + O_2 \rightarrow 2SO_3.$$
$$2H_2SO_3 + O_2 \rightarrow 2H_2SO_4.$$

The *removal of hydrogen* from hydrogen chloride, for the purpose of preparing chlorine, was (p. 109) likewise defined as oxidation:

$$O_2 + 4HCl \rightarrow 2H_2O + 2Cl_2.$$
$$2KMnO_4 + 16HCl \rightarrow 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2.$$

Every oxidation is accompanied by a reduction of the oxidizing agent. Thus, in the above instances, the free oxygen is reduced to water. The permanganate is also reduced, as we can see by the fact that its oxygen has been removed.

The appearance of a product that could only be formed by reduction is sometimes the first thing that calls our attention to the fact that an oxidizing action has occurred. When concentrated sulphuric acid acts upon carbon (p. 225), the CO_2 given off shows that there was oxidation, but the *odor* of the sulphur dioxide is the first thing we notice when doing the experiment:

$$2H_2SO_4 + C \rightarrow CO_2 + 2H_2O + 2SO_2.$$

Removal of the elements of water, for example from an oxacid like carbonic acid, is *neither oxidation nor reduction,* for hydrogen and oxygen are *both* removed:

$$H_2CO_3 \rightarrow CO_2 + H_2O.$$
$$H_2SO_3 \rightarrow SO_2 + H_2O.$$
$$NH_4OH \rightarrow NH_3 + H_2O.$$

The examples in the present chapter introduce nothing new. Ozone, hydrogen peroxide, and hypochlorous acid are oxidizing *agents,* like potassium permanganate. But the actions are simpler than are those of the latter substance.

We can now see that oxidation, *in these cases*, consists always in adding oxygen or removing hydrogen.

379. Other Cases of Oxidation. But oxygen is only one of a class of elements which we call non-metallic or negative elements, so that we do not *restrict* the term "oxidation" to actions involving oxygen. Thus, forming a chloride, by throwing a metal into chlorine, is oxidation also:

$$2Sb + 3Cl_2 \rightarrow 2SbCl_3.$$

Similarly, changing ferrous chloride $FeCl_2$ to ferric chloride $FeCl_3$ is oxidation:

$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3.$$

In every compound one of the elements is relatively positive and the other relatively negative. Iron is positive, and chlorine negative. In carbon monoxide carbon is (relatively) positive and oxygen negative. In ferrous sulphide iron is positive and sulphur (relatively) negative.

Oxidation, then, is **introducing, or increasing the proportion of the negative element, or removing, or reducing the proportion of the positive element** (see also §§ 380, 381). Reduction is the converse.

380. Oxidation and Valence. Combining oxygen or chlorine with a metal raises the *active* valence of the latter from zero to some finite value. *Metallic* copper has no valence *in use.* In $CuCl_2$ the copper is employing the valence II. The copper has been oxidized. Similarly, changing $FeCl_2$ to $FeCl_3$ increases the active valence of the iron from II to III. Conversely, changing HCl to Cl_2 alters the active valence of the chlorine from I to zero. Hence, **oxidation** may be defined as **increasing the active valence of a positive element or decreasing that of a negative element.** Reduction is the converse.

381. Oxidation and Electrons. Finally, since increasing the valence of a negative atom means adding one or more electrons to that atom, and increasing the positive valence of an atom means removing one or more electrons, we reach the *briefest* definition by saying: **oxidation is removing electrons and reduction is adding electrons.**

382. Energy and Chemical Action. It will have been noticed that there are two kinds of chemical actions: (1) those which, once started, proceed of themselves, and (2) those which have to be forced along by application of heat or some other form of energy. To the former kind belong most of the actions we use, such as combustion, displacements, and ordinary oxidation. These are accompanied by the liberation of energy in some form, usually heat. To the second class belong the decomposition of mercuric oxide, the electrolysis of salts and the formation of ozone. They are accompanied by absorption of energy, and they come to a stop when we cease supplying the energy.

Further than this, the actions which proceed of themselves *most rapidly* are generally those which give out *most* energy.

Finally, if free oxygen will not oxidize silver or indigo, we can accomplish the result by using a substance, like ozone or hypochlorous acid, capable of giving up energy when it liberates oxygen. The two lots of energy, being set free together, make a total liberation of energy sufficient to carry the whole action through successfully.

The chemically most active metals and oxidizing agents, therefore, are those which, in general, contain most available energy, and are therefore capable of liberating the most energy when they enter into chemical action.

383. Exercises.

1. Why does air containing ozone lose the latter (by change into oxygen) quicker when warm than when cold? State the law illustrated.

2. What other element, besides oxygen, have we found to occur in allotropic forms? Was the energy content of these forms different?

3. Make equations for: (a) the oxidation of carbon monoxide to carbon dioxide by ozone; (b) the action of the components of chlorine-water upon calcium hydroxide to give bleaching powder.

4. Mark the valences of the radicals in barium peroxide and hypochlorous acid.

5. By what experiments can we ascertain whether an acid is strong or weak?

6. What volume (at 0° and 760 mm.) of oxygen would be obtained by the decomposition of the hydrogen peroxide in 1 kilogram of the 3 per cent solution?

7. Are the following to be classed as oxidations: (a) the production of glucose from starch; (b) the action of heated cupric oxide on ammonia; (c) the action of magnesium on ammonia? If not, what is each?

CHAPTER XXV.

NITRIC ACID.

384. Nitric acid HNO_3 is used in large quantities for making explosives like guncotton, plastics like celluloid (Chap. XXXII), as well as innumerable drugs and dyes. Nitrates are largely used as fertilizers (p. 189, and §§ 571–572).

385. Manufacture. Nitric acid is obtained in two ways, namely by the action of sulphuric acid upon natural sodium nitrate and, to a smaller extent, by oxidation of the nitrogen of the atmosphere. The latter process will be referred to in a later section.

Sodium nitrate, Chile saltpeter, is found in an immense deposit (2 by 220 miles) on the boundary of Chile and Peru. This salt is mixed with concentrated sulphuric acid in iron retorts and gently heated to drive off the nitric acid. The sodium-hydrogen sulphate remains in the retort:

$$NaNO_3 + H_2SO_4 \rightleftarrows NaHSO_4 + HNO_3 \uparrow$$

The vapor is condensed in glass tubes (cooled with water) and the acid collected in vessels of earthenware. Sulphuric acid (b.-p. 338°) is used because it is much less volatile than nitric acid, and so only the latter is vaporized. The acid boils at 86° (760 mm.), but, to prevent loss by decomposition, a lower boiling-point is secured by reducing the pressure in the whole apparatus.

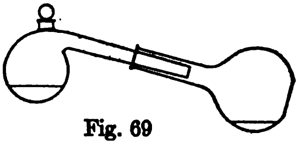
Fig. 69

In the laboratory the same action is employed, without, however, the reduction in the pressure (Fig. 69).

386. Physical Properties. Pure nitric acid is a colorless *liquid, boiling* at 86°. It is *miscible* in all proportions with water. The vapor, like hydrogen chloride gas, condenses moisture from the air, giving a fog of droplets of the solution. The concentrated nitric acid of commerce contains 68 per cent of the acid (32 per cent Aq) and boils at 120.5°.

387. Points About Oxacids. In dealing with an oxacid, there are some things which we must *acquire the habit* of keeping in mind.

Thus, an oxacid, as we have seen, can be deprived of water, leaving the *anhydride*. The chemist always thinks of the one as soon as the other is mentioned. If the acid is named, he instantly subtracts water from its formula to get the formula of the anhydride:

$$H_2CO_3 \rightarrow H_2O + CO_2.$$

Skeleton: $HClO \rightarrow H_2O + ?$

To balance the second equation, hydrogen atoms must be supplied *in pairs*, so the HClO must be multiplied by *two:*

Balanced: $2HClO \rightarrow H_2O + Cl_2O.$

The beginner must beware of making an arithmetical error either in multiplying HClO by 2 (which gives $H_2Cl_2O_2$), or in then subtracting H_2O. Absurd as it may seem, he is likely *not* to get Cl_2O, but some incorrect formula. With nitric acid the operation is similar:

Skeleton: $HNO_3 \rightarrow H_2O + ?$
Balanced: $2HNO_3 \rightarrow H_2O + N_2O_5.$

This operation should be practiced:

Skeleton: $HClO_4 \rightarrow H_2O + ?$ $H_3PO_4 \rightarrow H_2O + ?$
Balanced: $2HClO_4 \rightarrow H_2O + ?$ $2H_3PO_4 \rightarrow 3H_2O + ?$

The *valence of the characteristic non-metal is ascertained* by this process. What is the valence of Cl in HClO? The anhydride is Cl_2O. The valence is Cl^{I}. What is the valence of S in H_2SO_4? The anhydride is SO_3. The valence is S^{VI}. What is the valence of N in HNO_3? The anhydride N_2O_5 shows the valence to be N^{V}. What are the valences of Cl in $HClO_4$ and of P in H_3PO_4 and in HPO_3?

When we get SO_2 from sulphuric acid, by a chemical action, how do we know that the acid has been reduced (and something else oxidized)? Because in sulphuric acid we have $S^{VI}O_3^{II}$, and in the product $S^{IV}O_2^{II}$. The valence of S has been lowered from VI to IV. When *from* nitric acid we get N_2O_5, has there been reduction? No, because $N_2O_5 + H_2O = H_2N_2O_6 = 2HNO_3$ (nitric acid). If we get NO_2 or NO, has there been reduction of the acid? Yes, because the valence has been reduced: $N^{IV}O_2$, $N^{II}O$. We then proceed to pick out the other substance that has been oxidized.

Analyzing the formula of the acid, to get that of the anhydride, also *aids us to balance equations*, as we shall presently see.

388. Chemical Properties — Decomposition of Nitric Acid: Equation Making. The acid is *not very stable.* It decomposes, in part, even when simply distilled (86°), giving a red gas, **nitrogen tetroxide** NO_2, and oxygen:

Skeleton: $HNO_3 \rightarrow NO_2 + O_2 + ?$

We perceive at once that *water* must be formed as well:

Skeleton: $HNO_3 \rightarrow NO_2 + O_2 + H_2O.$
Balancing (partially): $2HNO_3 \rightarrow 2NO_2 + O_2 + H_2O.$

This gives us H_2O, correctly, but we have still only 6O on the left and 7O on the right:

Balanced: $4HNO_3 \rightarrow 4NO_2 + O_2 + 2H_2O.$

The operation becomes much simpler if we write the formula of the acid so as to show the anhydride:

$$2HNO_3\ (=H_2O,N_2O_5) \rightarrow 2NO_2 + O + H_2O.$$

We now see that each N_2O_5 will give $2NO_2 + O$, and to get O_2 we must double the whole:

$$4HNO_3 \rightarrow 4NO_2 + O_2 + 2H_2O.$$

This is the decomposition when the acid is heated by itself. *When a reducing agent is present,* oxides containing *less* oxygen than NO_2 may be formed. The oxides usually obtained are the tetroxide NO_2 and **nitric oxide** NO.

389. Nitric Acid as an Acid. Nitric acid turns blue litmus red, and is a *very active,* highly ionized *acid.* With bases it gives nitrates, which can be obtained from the solution by evaporation.

$$NaOH + HNO_3 \rightarrow H_2O + NaNO_3.$$
$$Ca(OH)_2 + 2HNO_3 \rightarrow 2H_2O + Ca(NO_3)_2.$$

390. Nitric Acid as an Oxidizing Agent. Since nitric acid gives up oxygen with liberation of energy, it is also active as an *oxidizing agent.* Glowing charcoal, as a powder or in the form of a stick, will burn when pure nitric acid is poured upon it (Fig. 70). Carbon dioxide and red nitrogen tetroxide NO_2 are evolved.

Fig. 70

Skeleton: $HNO_3 + C \rightarrow NO_2 + CO_2 + H_2O.$

Analyzed: $2HNO_3\ (= H_2O,N_2O_5) + C \rightarrow NO_2 + CO_2 + H_2O.$

Each N_2O_5 (from $2HNO_3$) will give $2NO_2 + O$. For CO_2, 2O is required, and therefore $4HNO_3$ is needed:

Balanced: $4HNO_3 + C \rightarrow 4NO_2 \uparrow + CO_2 \uparrow + 2H_2O.$

Nitric acid oxidizes indigo and other colored organic compounds, in the same way as do the three oxidizing agents described in the preceding chapter. It also oxidizes hydrochloric acid, upon which hydrogen peroxide does not act, so that it is a more active oxidizing agent than is that substance:

$$2HNO_3 + 6HCl \rightarrow 2NO + 4H_2O + 3Cl_2.$$

The mixture of concentrated hydrochloric acid, nitric acid, and water is called *aqua regia*, and has strong oxidizing properties, due to the presence of hypochlorous acid (from Cl_2+H_2O) as well as nitric acid.

391. Action of Nitric Acid on Metals. Magnesium, and metals *above* it in the activity list, will *displace* hydrogen freely, especially from diluted nitric acid:

$$Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2 \uparrow$$

But, with the less active metals, *oxidation* takes place, and instead of hydrogen, we get *water* and, of course, a reduction product of the nitric acid. The nitrate of the metal, however, is formed also. Even metals, like copper and silver, which do not displace hydrogen, are acted upon by nitric acid in the same way. For example, *diluted* nitric acid acts vigorously upon copper, giving nitric oxide NO as the reduction product:

Skeleton: $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O.$

If hydrogen could be displaced, the equation would be:

Partial (1): $Cu + 2HNO_3 \rightarrow Cu(NO_3)_2 + (2H).$

But nitric acid turns this to water instead, and each N_2O_5 gives $2NO + 3O$, or enough oxygen to oxidize 6H:

Partial (2): $2HNO_3 (= H_2O,N_2O_5) + 6H \rightarrow 3H_2O + 2NO.$

As hydrogen is not a product, and must cancel out, we now multiply Partial (1) throughout by 3, and add (1) and (2):

Partial (1)×3: $3Cu+6HNO_3 \rightarrow 3Cu(NO_3)_2+(6H).$
Partial (2): $(6H)+2HNO_3 \rightarrow 4H_2O+2NO.$
Balanced: $3Cu+8HNO_3 \rightarrow 3Cu(NO_3)_2+4H_2O+2NO.$

The nitric oxide is a colorless gas, but unites with oxygen in the air to give NO_2.

A **test for a nitrate** may be founded on this action. To the nitrate, sulphuric acid is added to liberate nitric acid. Then copper turnings are thrown in to give NO. A gas turning red as it meets the air shows that a nitrate was present.

392. Action Upon Organic Compounds. Nitric acid *stains* the skin and nails *yellow*, by giving colored compounds with the proteins. It gives similar compounds with wool (a protein), and therefore produces, on clothing, yellow stains which can not be removed.

The explosives made by the use of nitric acid are discussed in Chap. XXXII.

393. Nitric Oxide NO. This oxide is made by the action of diluted nitric acid upon copper, by the action already discussed (§ 391).

It is a *colorless* gas, and almost *insoluble* in water.

Vigorously burning phosphorus continues to burn in it:

$$4P + 10NO \rightarrow 2P_2O_5 + 5N_2.$$

Its most important property is that of *uniting with oxygen* to give nitrogen tetroxide (brownish-red gas):

$$2NO + O_2 \rightarrow 2NO_2.$$

394. Nitrogen Tetroxide NO_2. This oxide is formed by the union of oxygen with nitric oxide. It is given off, also, when *concentrated* nitric acid acts upon metals and other reducing substances. It is further produced, along with oxygen, when nitrates, excepting those of potassium and sodium are heated, dry:

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2.$$

Potassium and sodium nitrates, when heated, give off only oxygen, and leave the **nitrites**:

$$2KNO_3 \rightarrow O_2 + 2KNO_2.$$

Nitrogen tetroxide is a *brownish-red* gas. When cooled, it becomes pale yellow, and its *density* becomes twice as great. This is due to the formation of molecules of the formula N_2O_4:

$$2NO_2 \rightleftarrows N_2O_4.$$

The most interesting property of nitrogen tetroxide is its *action upon water*, whereby nitric acid is formed, and nitric oxide escapes:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO.$$

When oxygen is present also, then the NO gives more NO_2, and this in turn gives more nitric acid. This action plays an important part in the making of nitric acid from the nitrogen of the air (see § 395).

The gas is sometimes used for bleaching flour, but traces of the oxide remain in the bread.

395. Fixation of Atmospheric Nitrogen. Oxygen and nitrogen have no natural tendency to combine at the ordinary temperature, but rather the reverse — the compounds tend to decompose. But a high temperature will supply the necessary energy. Even so, however, the union extends to only 1 per cent of the mixture at 2000° and 5 per cent at 3000°:

$$N_2 + O_2 \rightleftarrows 2NO.$$

Nevertheless, owing to the cost, and limited supply of natural nitrates, machinery has been devised, and is now in successful use, for carrying on the combination on a commercial scale. Three devices are in use, and all employ hydro-electric power.

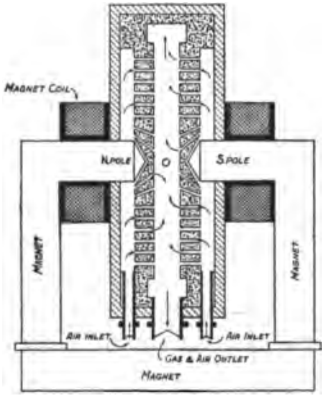

Fig. 71

In the **Birkeland-Eyde process** (Fig. 71), used at Notodden and elsewhere in Norway, an arc discharge between rods of carbon is spread, by the influence of powerful electromagnets, into a circular brush discharge several feet in diameter. The figure shows a cross section of the space filled by the discharge. In the center is a section of one of the carbon rods. Air is blown through the flame, giving 1 per cent of NO, and is cooled to permit of union of the nitric oxide with oxygen, to give the tetroxide, NO_2. The air containing NO_2 is then passed through absorbing towers down which water trickles. Here the action mentioned in the last section takes place, and an aqueous solution of nitric acid is produced. The yield is 70 g. of nitric acid per kilowatt-hour, and the net earnings in 1911 were $350,000. The nitric acid is mixed with calcium hydroxide (slaked lime):

$$Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O$$

to give calcium nitrate, which, being very soluble, is sold for use as a fertilizer.

The **Badische process,** used in the same factories in Norway, employs a discharge through a tube 22 feet long (Fig. 72). The column of air rotates as it traverses the tube and so every part is exposed to the discharge.

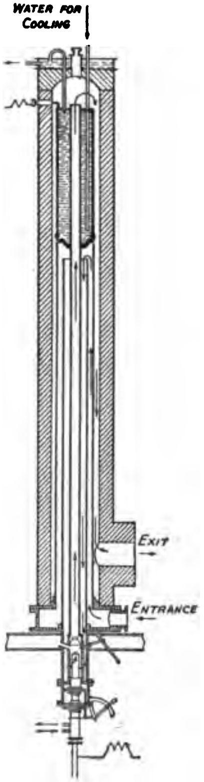

Fig. 72

The **Pauling process,** used at Gelsenkirchen, Germany, and Nitrolee, So. Carolina, uses preheated air, and a different arrangement of the discharge. The principles employed are, however, the same.

Other reactions involving the fixation of atmospheric nitrogen are discussed under calcium cyanamide (§ 536) and "root nodules" (§ 572).

396. Nitrous Acid HNO_2 and Nitrous Anhydride N_2O_3. When an acid, such as sulphuric acid, is added to a solution of a nitrite like potassium nitrite (§ 394), **nitrous acid HNO_2** is formed:

$$2KNO_2 + H_2SO_4 \rightarrow K_2SO_4 + 2HNO_2.$$

Nitrous acid, however, like sulphurous acid, is unstable and **nitrous anhydride** N_2O_3 is at once liberated and escapes as a gas:

$$2HNO_2 \rightarrow H_2O + N_2O_3 \uparrow$$

This gas is used as a catalytic agent in the chamber process (§ 361) for making sulphuric acid. The acid and its anhydride are employed in the manufacture of many dyes.

397. Nitrous Oxide N_2O. When ammonium nitrate, a white salt, is heated, it decomposes into steam and nitrous oxide:

$$NH_4NO_3 \rightarrow 2H_2O \uparrow + N_2O \uparrow$$

Nitrous oxide is somewhat more easily liquefied (b.-p. −90°) than is carbon dioxide. At 12° its vapor pressure is 41 atmospheres. It is sold, as a liquid, in steel cylinders, and used as an anæsthetic for minor operations, chiefly in dentistry. The hysterical symptoms which accompany its use caused it to be named "laughing gas."

Like oxygen, it relights a glowing splinter of wood, and supports combustion brilliantly. It does not interact with nitric oxide (§ 393), as does oxygen, however, to form nitrogen peroxide.

398. Exercises.

1. What is the valence of carbon in carbonic acid H_2CO_3?

2. What is the anhydride of nitrous acid HNO_2, and what the valence of nitrogen in this compound?

3. When nitric acid acts upon copper, which substance is oxidized and which reduced? State the effect upon the copper in terms of electrons.

4. How could you show experimentally that both nitrogen peroxide and oxygen are formed when cupric nitrate is heated?

5. How could you distinguish nitric oxide, (a) from hydrogen, (b) from oxygen?

6. How could you distinguish nitrous oxide from oxygen?

7. Make a list of the names and formulæ of the oxides of nitrogen, arranging them in the order of increasing proportions of oxygen.

8. How should you make ammonium nitrate (§ 326)?

CHAPTER XXVI.

THE HALOGEN FAMILY.

399. The elements, if we may judge from those studied or mentioned thus far, may be divided into two classes — the metallic or positive elements, like sodium, zinc, iron and magnesium, and the non-metallic or negative elements, like oxygen, sulphur, nitrogen and chlorine. The former give positive ions Na^+, Zn^{++}, Fe^{++}, Mg^{++}. The latter do not behave as positive ions. In other words, although we have nitrates and sulphates of all the *metals*, we have no nitrate or sulphate of oxygen or nitrogen.

400. Natural Families of Elements. We have a simple means of subdividing *within* each of these two classes. We can place together the elements of like valence. Thus Na^+ and K^+, or Zn^{++} and Mg^{++} resemble one another in two respects — metallic character and valence. Also, $O^=$ and $S^=$ form one group and Cl^-, Br^-, I^- and F^- form another. Groups of this kind are often spoken of as **natural families** of elements. The last group is called the **halogen family,** from the Greek for *salt-producing,* because these elements combine with sodium to give substances all resembling common salt. Usually, the elements of one family resemble one another in a number of ways, and show at the same time a gradation in properties which it is interesting to study.

401. The Halogen Family. The halogens are all negative elements, and univalent. They show a gradation in properties *which follows the order of their atomic weights.* Here are a few properties, as examples:

Element.	At. wt.	State.	B.-p.	Color.	Solubility (15°) in 1 c.c. Aq.	Heat of formation K compound.
Fluorine..........	19.0	gas	−187°	yel. (liq.)	....	118,100
Chlorine..........	35.5	gas	− 34°	or.-yel. (liq.)	0.072	104,300
Bromine..........	79.9	liq.,	59°	brown	0.032	95,100
Iodine............	126.9	solid	184°	violet	0.00015	80,100

It will be seen that, as the atomic weight increases, the boiling-point (b.-p.) rises, the color deepens, the solubility diminishes, and the heat of union with one atomic weight potassium becomes smaller. The last, and the atomic weight, are chemical properties, and they place the elements in the same order as do the physical properties.*

BROMINE Br.

402. The element was discovered by Balard in 1826 and derives its name from its offensive odor (Greek, *a stench*).

403. Preparation. The salt deposits and natural salt wells of Cheshire, of Germany, and of Michigan, West Virginia, Ohio, and Connecticut, contain some bromides, along with large quantities of common salt. When the latter has been largely separated by evaporation and crystallization, the bromides of sodium and magnesium, which are more soluble, collect in the mother liquor.

The bromine can be liberated at the positive electrode by electrolysis. But usually a chemical process is employed.

In Germany chlorine gas is dissolved in the liquor. This displaces the bromine, and the latter can be distilled out by heating:

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2.$$

$$2Br^- + Cl_2 \rightarrow 2Cl^- + Br_2.$$

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* For a complete table of all the families of elements, see the table of the Periodic System, facing the table of atomic weights (inside rear cover).

In the United States oxidation by pulverized manganese dioxide and sulphuric acid is generally employed, and this method can be used in the laboratory (Fig. 69, p. 240). The two reagents give manganous sulphate and oxygen:

$$\begin{array}{ll}
\textit{Partial (1):} & H_2SO_4 + MnO_2 \rightarrow MnSO_4 + H_2O + (O). \\
\textit{Partial (2)} \times \textit{2:} & 2H_2SO_4 + 2NaBr \rightarrow 2NaHSO_4 + 2HBr. \\
\textit{Partial (3):} & (O) + 2HBr \rightarrow H_2O + Br_2 \\
\hline
\textit{Balanced:} & 3H_2SO_4 + MnO_2 + 2NaBr \rightarrow MnSO_4 + \\
 & \qquad 2NaHSO_4 + 2H_2O + Br_2.
\end{array}$$

404. Physical Properties. Bromine is a liquid of a deep red-brown *color* and the vapor, of the same color, has a suffocating *odor*. It *boils* at 59°. It is moderately *soluble* in water, giving a 3.2 per cent solution (**bromine-water**), and is very soluble in carbon disulphide. The *density* of the vapor gives it the formula Br_2. Great care must be used in handling bromine, as, when spilt upon the skin, it kills the tissues and the sore is very liable to become infected.

405. Treatment of Burns. Burns made by bromine or strong acids should be washed instantly with water and then with bicarbonate of soda solution, and covered thickly with vaseline, or a salve of boric acid in lanoline, to protect them from infection.

406. Chemical Properties. A jet of burning *hydrogen* will continue to burn in bromine vapor, giving hydrogen bromide, which fumes in moist air like hydrogen chloride:

$$H_2 + Br_2 \rightarrow 2HBr.$$

Many of the *metals*, when thrown in the form of powder, leaf, or foil, into bromine vapor, combine directly, giving bromides. The action is similar to that with chlorine, but less vigorous.

407. Hydrogen Bromide HBr, Preparation. Hydrogen and bromine vapor unite rather slowly, and this direct union could at best be used only to get a jarful of the gas, mixed with excess of one or other of the ingredients. A stream of the pure gas is easily made by moistening red phosphorus with water, and allowing bromine to fall drop by drop into the paste (Fig. 73). To absorb the bromine vapor, carried by the gas, the latter is passed through a U-tube containing dry red phosphorus mixed with broken glass or beads:

$$2P + 3Br_2 \rightarrow 2PBr_3.$$
$$PBr_3 + 3H_2O \rightarrow 3HBr \uparrow + H_3PO_3.$$

The bromine forms phosphorus tribromide, which is immediately decomposed by the water. The phosphorous acid H_3PO_3 remains, dissolved in the water, in the flask. The gas can be collected by upward displacement of air.

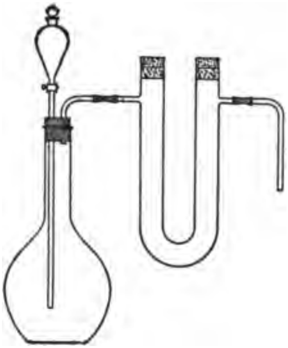
Fig. 73

It might seem that a simpler action would be that of sulphuric acid upon a bromide:

$$H_2SO_4 + KBr \rightarrow KHSO_4 + HBr.$$

This action takes place, but hydrogen bromide, being less stable than HCl, which *is* made upon this plan, is oxidized by the concentrated sulphuric acid, so that, although some of the gas escapes oxidation, it is mixed with much free bromine and sulphur dioxide: $H_2SO_4 + 2HBr \rightarrow SO_2 + 2H_2O + Br_2$. This action, indeed, enables us to *recognize* a bromide, by the color of the bromine vapor and the fuming of the hydrogen bromide produced. A more delicate test is mentioned below.

408. Properties of Hydrogen Bromide. The gas, like hydrogen chloride, is *colorless*, and has an irritating effect when *breathed.* It is extremely *soluble* in water, and fumes in moist air.

Chemically, hydrogen bromide is *stable*, though not so much so as hydrogen chloride. Its aqueous solution is an *active acid.* As such, it gives double decompositions with bases and salts. In these actions the bromides, if insoluble, are precipitated. Thus, with a salt of silver, we get a cream-colored precipitate

$$AgNO_3 + HBr \rightarrow AgBr \downarrow + HNO_3$$

of silver bromide (used on photographic plates and films).

Chlorine-water, added to a solution of any bromide, displaces the bromine, which may be recognized by its brown color (**test** for a bromide):

$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2.$$

A few drops of carbon disulphide, shaken with the mixture, will settle to the bottom, carrying the brown bromine with it in a more concentrated, easily recognizable form.

409. Uses of Compounds of Bromine. Bromine is manufactured in large amounts in Germany and in the United States. It is employed to make potassium bromide, and other bromides. These are utilized in medicine, and to precipitate silver bromide in the manufacture of photographic films and plates.

IODINE I_2.

410. Sources. Iodine was formerly all obtained from seaweed (kelp), certain species of which use the traces of organic compounds of iodine in sea water as part of their food. The dried seaweed is carbonized in retorts, and sodium iodide remains in the residue, along with much sodium carbonate and carbon. In an improved process the iodine compounds are dissolved out of the kelp, and from the latter a sort of gelatin, named **algin,** is extracted.

The greater part of our supply of iodine is at present obtained from potassium iodate KIO_3, which forms about 0.2 per cent of crude Chile saltpeter.

411. Preparation. The processes for obtaining iodine from the sodium iodide are precisely the same as those for bromine.

In France chlorine is used to displace the iodine:

$$Cl_2 + 2NaI \rightarrow 2NaCl + I_2 \downarrow$$

The precipitate of iodine is pressed free from the solution.

In Great Britain the iodide is mixed with manganese dioxide and sulphuric acid and heated:

$$3H_2SO_4 + MnO_2 + 2NaI \rightarrow MnSO_4 + 2NaHSO_4 + 2H_2O + I_2 \uparrow$$

Iodine vapor condenses upon a cold surface, not to the liquid, but directly to the solid, crystalline form. Distillation which gives a solid product is called **sublimation.** The crude iodine is purified by repetition of this process.

412. Physical Properties. Iodine forms *black*, shining *crystals*. The vapor, visible even at the ordinary temperature, is *violet* in color (hence the name of the substance, from Greek, meaning *like a violet*) and has a *density* corresponding to the formula I_2. The substance is very slightly *soluble* in water. It dissolves, however, easily in carbon disulphide (violet solution), in alcohol or potassium iodide solution (brown solution), and even in starch, upon which a trace of it confers a strong blue color (*test* for free iodine; see also § 415). These colors are shown only by free iodine — the iodides are colorless and do not act upon these solvents.

413. Chemical Properties. Iodine unites very slowly and incompletely with *hydrogen*, giving hydrogen iodide. It combines readily with *phosphorus* (PI_3), and with many of the *metals*, giving iodides.

414. Hydrogen Iodide, Preparation. The gas is prepared by the process used for hydrogen bromide. Red phosphorus and iodine are mixed, and water is allowed to fall drop by drop upon the mass (Fig. 73, p. 253):

$$2P + 3I_2 \rightarrow 2PI_3.$$
$$PI_3 + 3H_2O \rightarrow 3HI + H_3PO_3.$$

The gas is very dense (HI = 1 + 127 = 128 g. per 22.4 liters, against 28.95 g. for air) and can be collected by upward displacement of air.

The action of sulphuric acid upon an iodide does not give pure hydrogen iodide, because most, though not all, of the latter is oxidized by the sulphuric acid. Hydrogen iodide, being much less stable than even hydrogen bromide, is a more active reducing agent, and reduces the sulphuric acid to hydrogen sulphide. The odor of this gas is therefore very conspicuous when an iodide is moistened with sulphuric acid:

$$NaI + H_2SO_4 \rightarrow NaHSO_4 + HI.$$
$$H_2SO_4 + 8HI \rightarrow H_2S + 4H_2O + 4I_2.$$

The violet vapor of iodine becomes visible if the test-tube is warmed. A rough *test* for an iodide is afforded by this action.

415. Properties. Hydrogen iodide is exceedingly *soluble* in water, and fumes strongly in moist air. It is *colorless.*

The aqueous solution is an active acid. The iodide-ion I^-, which it contains, gives precipitates of insoluble iodides, like the yellow silver iodide AgI:

$$Ag^+ + I^- \rightarrow AgI \downarrow$$

Chlorine-water or bromine-water, added to a solution of this or any other iodide, displaces the iodine:

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2.$$

The free iodine, even if present in minute amounts, may be *recognized* by shaking the liquid with a few drops of carbon disulphide. The iodine gives a violet solution in the latter. A still more delicate *test* is the addition of a drop of very thin starch paste, which gives a deep-blue tint with *free* iodine. Filter paper dipped in starch paste and dried can also be used, by touching it with the solution containing the free iodine.

416. Uses of Iodine and Its Compounds. The alcoholic solution (tincture of iodine), painted over the skin, is used as an antiseptic before operations. It also reduces swellings and inflammation. **Iodoform** CHI_3 is a solid used for purposes similar to those last mentioned. **Iodothyrin** is an organic compound found in the human thyroid gland, as well as that of other animals. An extract of sheeps' thyroids is administered with remarkable success in cases of degeneration, associated with abnormally small natural development of the gland (cretinism). Silver iodide is contained in the coating on photographic plates and films.

FLUORINE F_2.

417. Compounds of fluorine are found in large quantities as minerals, but the compounds are so stable that the element is very difficult to liberate. The natural compounds, however, have many important uses.

418. Occurrence. Calcium fluoride CaF_2 **(fluorite)** occurs in nature in beautiful cubical crystals. **Cryolite** $AlF_3, 3NaF$ is used in the modern manufacture of aluminum (§553). **Apatite** $Ca_5(PO_4)_3F$ is a common constituent of rocks and soils. When slowly decomposed, by weathering, it furnishes soluble phosphates. These are absorbed by plants, for which they are a necessary food.

419. Preparation of Fluorine. The element is obtained by electrolysis of potassium-hydrogen fluoride KHF_2 dissolved in liquefied hydrogen fluoride. The electrodes are made of an alloy of platinum and iridium, with which fluorine has little tendency to combine. The vessel is a U-tube of copper (Fig. 74) and, to prevent vaporization of the hydrogen fluoride (b.-p. 19.4°), is kept at −23° to −40° during the operation. Hydrogen is liberated at one pole and fluorine at the other. After long and fruitless trial of other methods by many chemists, this one was discovered by Moissan (1886).

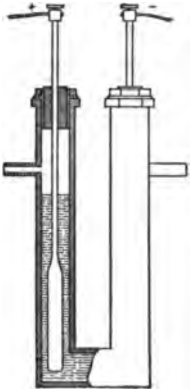
Fig. 74

420. Properties. Fluorine is a *yellow* gas, with a *density* greater than that of air (G.M.V. weighs 38 g.). It is the most difficult of the halogens to *liquefy* (b.-p. −187°).

Fluorine is the most *active* of the non-metals. It *combines* with *all the metals*, but most slowly with the platinum metals and with gold. In the preparation of the gas the copper is protected from serious attack by the layer of fluoride first formed. Fluorine combines also with *hydrogen* in the cold and, unlike chlorine, without the assistance of light. It combines with most of the *non-metals*, but not with oxygen, chlorine, nitrogen, or the indifferent gases of the atmosphere.

With water (vapor or liquid) fluorine interacts, giving a deep-blue gas, ozone, and hydrogen fluoride H_2F_2:

Skeleton: $F_2 + H_2O \rightarrow H_2F_2 + O_3$.

Balanced: $3F_2 + 3H_2O \rightarrow 3H_2F_2 + O_3$.

421. Hydrogen Fluoride H_2F_2, Preparation. When pulverized calcium fluoride and concentrated sulphuric acid are placed in a retort of platinum or lead and the mixture is warmed, hydrogen fluoride passes over. The vapor is usually led into water, in which it is very soluble (hydrofluoric acid):

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + H_2F_2.$$

The acid is kept in bottles of paraffin or rubber, as glass interacts with it rapidly.

422. Physical Properties. The vapor of hydrogen fluoride can be condensed to a colorless *liquid* boiling at 19.4°. Being very *soluble*, it fumes strongly in moist air. The vapor *density* below 40° corresponds with the formula H_2F_2, but at higher temperatures gradual dissociation to HF occurs.

423. Chemical Properties. The aqueous solution has all the properties of an *acid*. The substance has, in addition, the remarkable property of acting upon *silica* SiO_2 (sand), and silicates, to give **silicon tetrafluoride** SiF_4 (a gas). Hence it attacks glass, which is a mixture of sodium silicate and calcium silicate:

$$SiO_2 + 2H_2F_2 \rightarrow SiF_4 + 2H_2O.$$
$$CaSiO_3 + 3H_2F_2 \rightarrow SiF_4 + CaF_2 + 3H_2O.$$

Thus, when glass is covered with melted paraffin to protect the surface, and marks or letters are made by removing the paraffin with a sharp instrument, hydrogen fluoride will decompose the glass at the parts thus exposed (*test* for fluorine). In this way the graduation on thermometer stems and lettering on glass are frequently made. The vapor gives rough, easily visible depressions, the solution smooth, glossy ones.

On account of this property, hydrofluoric acid is used for removing adhering sand from castings and for cleaning the outsides of granite and sandstone buildings.

THE HALOGENS AS A FAMILY.

424. In the opening paragraphs of this chapter (p. 251) it was shown that the heat of combination of potassium with the halogens was greatest with fluorine, and least with iodine. The affinity of the halogens for all positive elements diminishes in the order F, Cl, Br, I, that is as the atomic weight of the halogen increases.

We have learned also that chlorine displaces bromine and iodine from bromides (p. 254) and iodides (p. 256). In like manner, bromine displaces iodine. It may be noted that oxygen displaces iodine from hydriodic acid, and that all the halogens displace sulphur from sulphides. Thus an **order of activity for the non-metals** has been established, similar to the activity order for the metals. For the non-metals it is: **F, Cl, Br, O, I, S.**

Although the halogens thus show different degrees of activity, they are closely alike in their chemical nature. They are all univalent;* they are strongly negative or non-metallic; their hydrides are all active acids. They differ in two of these points from other non-metals, for oxygen and sulphur are bivalent (and the latter sexivalent also), and the hydrides of oxygen (H_2O) and of sulphur (H_2S) are very feeble acids.

425. Exercises.

1. Write the formulæ of the bromides, iodides, and fluorides of zinc, carbon, and aluminium.

2. How should you distinguish by chemical reactions the chloride, bromide, iodide, and fluoride, (a) of hydrogen, (b) of sodium from one another?

3. Write the equation for the action of iodine upon a solution of hydrogen sulphide.

4. Why does hydriodic acid, when left in the air, become brown in color?

5. Make a list of all the acids we have encountered, and note which are weak and which strong.

6. How should you make potassium bromide, starting with, (a) potassium and bromine, (b) hydrogen bromide, (c) potassium iodide?

7. What is the valence of chlorine in chloric acid (p. 260, footnote, and see p. 242)?

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* They are so when in binary combination with a metal: KBr, KI, $ZnBr_2$, etc. In oxygen compounds they often show a higher valence, as in $KClO_3$ and $HClO_3$ (chloric acid).

CHAPTER XXVII.

PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH.

P 31.
As 74,
Sb 120
Bi 208

426. In the preceding chapter we learned that the elements can be grouped in *families*,* and we became acquainted with one family, namely that to which chlorine belongs. We now take up the elements which, with nitrogen, form the **nitrogen family.** These elements all have two regular valences, being trivalent and quinquivalent. Nitrogen, phosphorus and arsenic are non-metallic elements, that is, they do not form positive radicals of salts. Antimony is non-metallic, although in its trivalent condition it acts also as a metallic element. Bismuth is metallic.

PHOSPHORUS P.

427. Occurrence. Calcium phosphate $Ca_3(PO_4)_2$ forms about 25 to 27 per cent of the material of the bones and teeth of animals. The same salt occurs in deposits, as a mineral, and is found scattered through all fertile soils. Complex organic compounds of phosphorus, such as lecithin, are essential constituents of the muscles, nerves and brains of animals and are found also in plants. The average man's skeleton contains 1400 g. of phosphorus, his muscles 130 g., and his nerves and brain 12 g. Amongst foods, egg-yolks and beans contain an unusually large proportion, nuts, peas, and wheat (entire grain) coming next.

Phosphorus was discovered by Brand in 1669, and by Kunkel in 1670, by distilling at a white heat the solid residue from evaporated animal matter. They were both search-

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*** All the families are shown in the table opposite the inside of the rear cover of this book.**

ing for the philosophers' stone. Scheele in Sweden prepared it from bones in 1771. The element is used chiefly in the manufacture of matches and, to a small extent, in roach paste and rat poison.

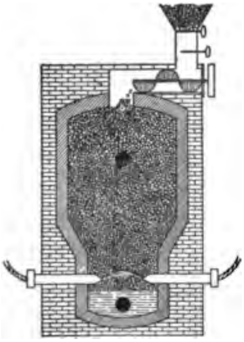
Fig. 75

428. Manufacture of Phosphorus. Phosphorus is now manufactured by mixing natural calcium phosphate with sand (SiO_2) and coke, and heating the mixture in an electric furnace (Fig. 75). The mixture is admitted by moving the traps below the hopper, and is carried into the furnace by the worm conveyor. The resistance of the mass between the electrodes causes great development of heat. The actions may be shown by partial equations, which, when added together, give the complete equation:

$$\begin{array}{r}
Ca_3(PO_4)_2 \rightarrow 3CaO + P_2O_5 \\
3CaO + 3SiO_2 \rightarrow 3CaSiO_3 \text{ (calcium silicate)} \\
P_2O_5 + 5C \rightarrow 2P + 5CO \\
\hline
Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 \downarrow + 2P \uparrow + 5CO \uparrow
\end{array}$$

The calcium silicate is melted and runs out below as a slag. The phosphorus (vapor) and carbon monoxide (gas) pass off through the opening near the top. The phosphorus vapor is condensed under cold water.

429. White Phosphorus. The product, after purification, is a *colorless*, transparent waxy solid (sp. gr. 1.83), which *melts* at 44° and *boils* at 287°. It is *insoluble* in water, but dissolves in carbon disulphide. It has a strong *odor*, resembling ozone.

White phosphorus *oxidizes* in the air, giving, when moist, phosphorous acid and phosphoric acid, and *emitting a faint light* from which the element derives its name (Greek, *light bearer*). It catches fire at a low temperature (about 35°), and in burning forms a cloud of the solid phosphorus pentoxide P_2O_5. It *combines* readily, even when cold, with the halogens, and when heated it unites with sulphur and the more active metals.

White phosphorus is a very active poison (fatal dose, 0.15 g.). When traces of the vapor are breathed day after day, a disease, frequently shown by workers in match-factories and consisting in ulceration of the bones of the jaw, makes its appearance. There is no longer any excuse for exposing the work people to the risk of contracting this horrible disease, for matches can now be made without the use of free, white phosphorus (see § 431 below). The use of white phosphorus is forbidden by law in Sweden, France, Great Britain, and Switzerland and is penalized by a special tax in the United States.

430. Red Phosphorus. When white phosphorus is heated to 230 to 300° in a tightly closed vessel (air excluded) it changes into **red phosphorus.** This material is composed of small crystals, of dull *red color*, and variable specific gravity 2.19 to 2.34. It is *insoluble* in carbon disulphide, has *no odor*, and is *not poisonous.* On distillation the vapor condenses to white phosphorus.

This allotropic form of phosphorus is formed from the white variety with liberation of much heat. It thus contains less energy, and is much less active. It burns to form the pentoxide, but has to be heated to about 240° before it will catch fire in the air. It combines also with elements other than oxygen much less readily than does white phosphorus.

431. Manufacture of Matches. These are of two kinds, ordinary matches, which strike on any rough surface, and "safety" matches. Ordinary matches are still made in some countries by dipping the splints of wood in melted paraffin, and then in a paste made of 4 to 7 per cent of white phosphorus, lead dioxide about 50 per cent, and dextrin (paste) or glue. The head, when dry, is dipped in varnish to exclude air and moisture. Where the use of white phosphorus is very properly forbidden, a sulphide P_4S_3 is substituted. When the match is struck, the friction explodes the mixture of phosphorus trisulphide (combustible) and lead dioxide (or other oxidizing agent), and the resulting heat sets fire to the paraffin and this, in turn, to the wood.

Safety matches carry no phosphorus, but only a mixture of substances containing oxygen, such as potassium chlorate and potassium chromate, with a combustible, like antimony trisulphide, some dextrin and a filling (*e.g.* chalk). The box is coated with a mixture of red phosphorus, antimony trisulphide, dextrin and filling. The friction converts a trace of the red phosphorus into the white variety, and the latter sets fire to the head.

432. Phosphorus Pentoxide P_2O_5. When phosphorus is burned in *dry* air or oxygen, under a bell jar, the cloud of pentoxide slowly settles as a white powder. If the pentoxide is thrown into cold water, chemical union takes place. The heat developed produces a hissing sound, caused by the formation and condensation of minute bubbles of steam. The solution when boiled, evaporated, and held at 30 to 40°, gives crystals of **orthophosphoric acid** H_3PO_4 (m.-p. 42°).

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4.$$

On account of its tendency to unite with water, the pentoxide is used for drying gases.

433. Phosphates of Calcium. It will be seen that natural calcium phosphate $Ca_3(PO_4)_2$ is the **orthophosphate of calcium.** It is found in considerable deposits in So. Carolina, Florida, Tennessee, and several western states, and in Algeria and Tunis. Since all plants contain organic compounds of phosphorus, they must find a continuous supply in the soil, otherwise their growth will cease. Hence, when the proportion present is too small, calcium phosphate is frequently added as a fertilizer. Since, however, plants can absorb solutions through their roots, *but not solids*, this insoluble salt affords only an exceedingly dilute phosphorus diet. Hence, a more soluble compound is to be preferred. This is found in **calcium acid-phosphate** (" superphosphate ") $CaH_4(PO_4)_2$, which is made by heating pulverized natural calcium phosphate with sulphuric acid, containing the requisite proportion of water:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \rightarrow CaH_4(PO_4)_2 + 2CaSO_4,2H_2O.$$

The whole turns into a dry mixture, consisting of the superphosphate and gypsum (hydrated calcium sulphate). The latter does not interfere with the fertilizing power of the soluble superphosphate, so the mixture is placed directly in sacks and sold as "superphosphate of lime."

In slaughterhouses the bones, after being deprived of fat and gelatin, give a residue containing much calcium phosphate. This residue is treated with sulphuric acid and made into fertilizer.

434. Test for a Phosphate. Most phosphates (and phosphoric acid), when mixed intimately with dry sodium carbonate, charcoal, and magnesium powder, and heated in a narrow tube closed at one end, give a phosphide of the metal (Na_3P or Mg_3P_2). When the mass is moistened, the odor of **phosphine** PH_3 can be recognized.

$$Na_3P + 3H_2O \rightarrow 3NaOH + PH_3 \uparrow$$

435. Phosphorus and Nitrogen Compared. Although the simple substances, phosphorus and nitrogen, have little in common, they form compounds of similar composition, which are in many ways alike. Thus we have ammonia NH_3 and

phosphine PH_3, both gases. Then there are the oxides N_2O_3 and N_2O_5, to which the oxides P_2O_3 and P_2O_5 correspond. All these oxides are anhydrides of acids. Both nitrogen and phosphorus are typically non-metallic elements (p. 250), entering into negative radicals. Both elements are trivalent in one series of compounds (NH_3,N_2O_3, PH_3, P_2O_3) and quinquivalent (N_2O_5, P_2O_5) in another series. For these and other reasons they are classified in the nitrogen family of elements.

ARSENIC As.

436. Arsenic, the third member of this family, is metallic in *appearance* and in *physical* properties, although in combination it behaves as a non-metallic element. The metal is used, with lead, in making small shot, and the oxide As_2O_3 in preparing medicines and insecticides.

437. Preparation. A mineral similar to pyrite FeS_2, but containing arsenic in place of half of the sulphur, **arsenical pyrites** FeSAs, is the commonest natural form of arsenic. When this mineral is heated (air excluded), arsenic passes off as vapor and condenses as a crystalline metallic powder:

$$FeSAs \rightarrow FeS + As \uparrow$$

Most natural sulphides (PbS, FeS_2, SnS_2, $CuFeS_2$, etc.) contain more or less arsenic, which takes the place of a part of the sulphur. When these ores are oxidized in a draft of air (roasted), as one step towards the ultimate extraction of the metal, the metal, sulphur, and arsenic are all converted into oxides. The sulphur dioxide passes off as gas, but the arsenic trioxide As_2O_3, a solid, settles in the flues. By distilling the deposit with carbon, free arsenic is obtained:

$$As_2O_3 + 3C \rightarrow 2As \uparrow + 3CO \uparrow$$

438. Properties and Uses. The element has a *silvery luster*, but tarnishes quickly. When it is heated, its vapor reaches a pressure of 760 mm. before the melting-point is attained, so that the metal distils without melting.

The metal *burns* in air with a bluish-white flame, giving clouds of white particles of the trioxide As_2O_3 (poisonous).

In the making of **small shot**, about 0.5 per cent of arsenic is added to the lead. The latter is then run into a vessel, with a perforated bottom, placed at the top of the shot tower. The arsenic, like any dissolved substance (p. 91), lowers the freezing-point of the solvent (lead), and delays the solidification of the lead until the drops have assumed perfect spherical form. At the foot of the tower the drops fall into water and are cooled. The arsenic also renders the metal harder than pure lead, and less apt to be deformed during the explosion of the cartridge.

439. Arsenic Trioxide As_2O_3. This oxide, formed when arsenic burns, is a *white* crystalline powder. It is *acidic* and forms salts with bases. **Paris green** and **Scheele's green** are made by dissolving the oxide in boiling water and adding a salt of copper. They are green, insoluble compounds used, as insecticides, for spraying plants. Because of their poisonous nature, they are no longer employed as ingredients in paints.

Arsenic trioxide (**white arsenic**) is the poison most commonly used for criminal purposes, yet it is one of the easiest poisons to detect in the body after death. It is contained in "Fowler's solution" which is used as a heart tonic.

440. Arsenic as a Member of the Nitrogen Family. While free arsenic is as different physically from phosphorus as the latter is from nitrogen, the *compounds* have much in common. Arsenic forms **arsine** AsH_3 (corresponding to NH_3 and PH_3) and arsenious oxide As_2O_3 and **arsenic oxide** As_2O_5, and the acids H_3AsO_3 and H_3AsO_4. In these compounds it is nonmetallic, and shows the valences three and five.

ANTIMONY Sb.

441. Preparation and Properties. Antimony is found free in nature. The sulphide, **stibnite** Sb_2S_3, is also a well-known mineral. When the latter is melted with iron, ferrous sulphide and free antimony are formed.

$$3Fe + Sb_2S_3 \rightarrow 2Sb + 3FeS.$$

The molten ferrous sulphide (sp. gr. 4.8) floats upon the molten antimony (sp. gr. 6.5), and the products, being mutually insoluble, are easily separated.

The metal is brilliantly *silvery* and non-tarnishing. It is *brittle* and the black powder obtained by pulverizing it, "antimony black," is rubbed on plaster casts to give them a dull, metallic appearance. When heated, antimony volatilizes and *burns* in the air with a brilliant white light to form the white **trioxide** Sb_2O_3.

The **trisulphide** Sb_2S_3 (orange-colored when precipitated) is used in making matches and fireworks.

442. Alloys Containing Antimony. The metal is chiefly used as an ingredient in alloys. Lead, when solidifying, shrinks and antimony counteracts this tendency. Hence **type metal,** which, when cold, must fill the mould completely, is made by melting together 15 to 25 per cent of antimony, 10 to 20 per cent tin, and the rest lead. The alloy is also harder than lead, and is less quickly deformed by handling and by use in the printing press.

Babbitt's Metal (Sb 3, Zn 69, As 4, Pb 5, Sn 19), and other **anti-friction alloys,** used in lining bearings, contain antimony along with zinc, copper, and other metals. Molten mixtures of metals (alloys), when solidifying, do not always form a homogeneous, solid mass. In an anti-friction alloy, what is wanted is a mass, in general soft, but containing hard particles. The latter bear most of the pressure, yet, as the alloy wears, *they are pressed into the softer matrix* so that a smooth surface is always presented. An alloy which has the opposite composition, that is, which gives a hard mass containing softer particles, develops heat by friction much more rapidly.

BISMUTH Bi.

443. As the atomic weight increases, the members of this family become more like metallic elements in their chemical properties. Thus bismuth is a true metallic element. Its oxides are basic, and its compounds give positive ions Bi^{+++} and include salts like the carbonate, sulphate, chloride, and phosphate.

444. Metallic Bismuth. The metal occurs free in nature. It is a *brittle* metal, with a *pink* metallic luster. It *melts* at 270° and vaporizes at a high temperature. It does not tarnish. It is used in preparing *alloys* with very low melting-points. Thus **Wood's metal** contains bismuth (m.-p. 270°) 4 parts, lead (m.-p. 326°) 2 parts, tin (m.-p. 233°) 1 part, and cadmium (m.-p. 320°) 1 part. As is the case with other solutions, the melting-point is lower than that of any of the components, namely 60°. Alloys of this class are used as plugs in sprinkler systems and stops to hold steel fire-doors open. When, in consequence of a fire, the temperature rises, the alloy melts, the water exits are opened and the fire-doors swing shut. Safety plugs in steam boilers, made of a similar, but less fusible alloy, melt when, as the result of failure of the safety valve, the steam pressure, and therefore the temperature, exceeds a predetermined value. They behave in the same way when the water is dangerously low and the metal above the water becomes too hot.

445. Compounds of Bismuth. When strongly heated, the metal *burns* to form a brown trioxide Bi_2O_3. This oxide gives salts with acids. Thus, with nitric acid it dissolves to form a solution of **bismuth nitrate:**

$$Bi_2O_3 + 6HNO_3 \rightarrow 2Bi(NO_3)_3 + 3H_2O.$$

When the solution is evaporated, the nitrate appears in colorless crystals. If the crystals are placed in water, a white, insoluble basic nitrate is formed:

$$Bi(NO_3)_3 + H_2O \rightleftarrows BiONO_3 \downarrow + 2HNO_3.$$

This is used in medicine under the name of **bismuth subnitrate.** The action is reversible, so that, when excess of nitric acid is added, a clear solution of the trinitrate is formed.

446. Exercises.

1. By what chemical experiments could you recognize red phosphorus?
2. Explain the fact that solid Wood's metal floats upon melted Wood's metal.
3. Why is white phosphorus always kept under water?

CHAPTER XXVIII.

SILICON AND BORON.

447. Silicon belongs to the carbon family, being, like carbon, quadrivalent and non-metallic.

Although silicon does not occur free in nature, yet its compounds are so plentiful that about 26 per cent of the terrestrial globe is silicon. Instead of naming all the rocks which contain it, such as sandstone, basalt, granite, and so forth, it is easier to say that limestone is the only common rock which is *not* siliceous.

448. Silicon Si. The element is now manufactured at Niagara Falls and elsewhere, by heating sand (SiO_2) with coke in an electric furnace. The process closely resembles that for making carborundum (p. 153), except that less coke is used:

$$2C + SiO_2 \rightarrow 2CO \uparrow + Si.$$

The element, as prepared in this way, is a grey, crystalline material.

449. Silicon Dioxide SiO_2 (Silica), Physical Properties. Colorless rock-crystal, often showing large hexagonal crystals (Fig. 3, p. 4), is pure silicon dioxide, deposited from natural solutions. When impurities enter into it, smoky quartz, rose quartz (pink), and amethyst (violet) are formed. Often the impurity changes during the growth of the deposit, and beautifully variegated specimens, like jasper, catseye, and agate are produced. Chalcedony, opal, and flint contain a small amount of water in combination. The nodules (rounded masses) of flint break in splinters, when struck, and our prehistoric ancestors dexterously fashioned their implements and weapons from this material. The solid structure of sponges and diatoms is also hydrated silicon dioxide. The tests of the latter organisms constitute **infusorial** or **diatomaceous earth** (**Tripoli**) — used in making polishing powders and for removing coloring matters from oils.

450. Chemical Properties. Silicon dioxide (sand) is not acted upon by acids, with the exception of hydrofluoric acid, which gives **silicon tetrafluoride** SiF_4 (p. 259) and water:

$$SiO_2 + 4HF \rightarrow SiF_4 \uparrow + 2H_2O.$$

When silicon dioxide is fused with sodium carbonate, carbon dioxide is liberated, and **sodium silicate** Na_2SiO_3 is formed:

$$SiO_2 + Na_2CO_3 \rightarrow CO_2 \uparrow + Na_2SiO_3.$$

The resulting salt is very soluble in water and a strong solution of it, or rather of a disilicate $Na_2Si_2O_5$, is sold under the name of **water-glass** or soluble glass. This material is used as a filler in cheap soaps, as an ingredient in artificial stone, a coating to render wood or cloth fireproof, and a cement for uniting glass or porcelain. Eggs are preserved by being submerged in a solution of this salt (1 part sol. of sp. gr. 1.35 : 9 parts Aq).

When an acid is added to sodium silicate solution, **silicic acid** H_4SiO_4 (gelatinous) is precipitated. If this acid is heated, silica SiO_2 remains as a powder.

451. Glass. Calcium carbonate (limestone) interacts at a high temperature with sand in the same way as does sodium carbonate (§ 450):

$$SiO_2 + CaCO_3 \rightarrow CO_2 \uparrow + CaSiO_3$$

giving **calcium silicate.** Now sodium silicate, when alone, is soluble in water. Calcium silicate is insoluble, but forms a brittle, crystalline mass. By using *both* sodium and calcium carbonates, and employing a larger proportion of sand than that shown in the equation, a material is obtained which has the qualities required in glass. When cooled, the molten mass becomes viscous and finally, for all practical purposes, solid. Yet it does not crystallize—it is amorphous. It is also practically insoluble in water.

By pouring the viscous material into moulds, or stamping it with dies, articles of *pressed glass* are obtained. Bottles are *blown*, by taking up a sufficient mass of the hot, thick liquid on the end of an iron tube, inserting it in a mould, and blowing until the outline of the mould is filled. *Window glass* is made by blowing an immense, elongated bubble (6 by 1½ ft.), ripping it while still hot and soft, and flattening it out. *Plate glass* for windows and mirrors is manufactured by pouring out the material upon a cast-iron table, with a raised rim, and passing a large, heated iron roller over it. The plate is subsequently ground flat on both sides and polished with rouge (Fe_2O_3).

Soda-calcium glass is called **soft glass**, because it is easily softened by heating. When potassium carbonate is substituted for sodium carbonate, a less fusible substance, used in making some chemical apparatus, and called **hard glass**, is obtained. When lead oxide is employed in place of the limestone, a potassium-lead silicate $K_2SiO_3, PbSiO_3, xSiO_2$ is formed which, on being cooled, gives **flint glass**. This glass has a higher density and greater brilliancy than soft glass, and is used in making vessels of cut glass and lamp chimneys. The cutting is done with a revolving grinding wheel.

When glass is allowed to cool quickly, the product is very brittle and apt to crumble to pieces on receiving a shock or scratch. Glassware is therefore all **annealed**, by being passed on a slowly moving frame through a long furnace, which is very hot at the entrance and much cooler at the exit. During the passage, the molecules of the material adjust themselves to a stable arrangement.

Colored glass is made by adding oxides of metals which, with the silica, give colored silicates. Oxide of chromium gives green silicates, oxides of copper and of cobalt blue silicates, and oxide of manganese violet. Gold oxide is reduced to the metal, which goes into colloidal solution and gives ruby glass. Milky glass is made by adding calcium fluoride, or stannic oxide. The green color of bottle glass is due to iron (ferrous silicate) derived from impure sand or limestone.

The rough surface of **ground glass** is produced with a sand blast. For **engraved glass,** the surface is covered with paraffin to protect it from the sand blast, and only the pattern is left exposed.

In **granite iron ware** the surface is covered with a thin layer of easily fusible glass (enamel, see borax).

Pure quartz can be melted in the oxy-hydrogen blowpipe, and recently chemical apparatus (**silica ware**) has been made out of it. It has the advantage of being less soluble than glass, and of not breaking even when it is heated white hot and quenched in cold water. Glass breaks when chilled, because the parts first cooled shrink considerably and a great strain is produced. Quartz suffers very little change in volume with change in temperature, and so unequal cooling causes almost no strain.

BORON B.

452. The element boron resembles silicon and graphite in appearance. It has no applications.

453. Boric Acid H_3BO_3. This acid is contained in the steam which issues from the ground in certain parts of Tuscany. It is caught in water, placed in basins built over the "soffioni," and separated by evaporation. Much of it is also made from borax.

Boric acid crystallizes in *white*, slippery scales. It *dissolves* somewhat in water (4 : 100 at 18°), and the saturated solution, mixed with an equal volume of water, is used as an eye-wash, for example when the eyes have been irritated by dust. It is a mild *antiseptic*, and preserves foods by preventing the development of moulds and bacteria.

When heated, it gives **tetraboric acid**:

Skeleton: $H_3BO_3 \rightarrow H_2B_4O_7 + H_2O$

Balanced: $4H_3BO_3 \rightarrow H_2B_4O_7 + 5H_2O$

and eventually **boric anhydride B_2O_3.**

454. Borax. This salt, when crystallized from solution, combines with water to form a hydrate. As sold, it is therefore the deca-hydrate of **sodium tetraborate** $Na_2B_4O_7,10H_2O$.

It is made by adding calcium borate, found in California, to sodium carbonate solution. The precipitate of calcium carbonate is separated by filtration, and the solution is concentrated until crystals appear upon cooling.

It is a *white* crystalline salt. It is added to the glass, used for enamelling and glazing, to make it more fusible and easier to spread in a thin layer. It is a preservative. Since it contains but a small proportion of the metallic oxide (Na_2O, $2B_2O_3$), it *combines with other metallic oxides* when fused with them. For this reason the powdered salt is sometimes sprinkled on tarnished metallic surfaces which are to be soldered or brazed. The heat of the bolt or blowpipe melts the borax, and the latter removes the oxide and permits perfect running of the solder over the surface. The borates thus formed are often colored, and the colors afford a means of recognizing the metallic compound which produced them. In chemical analyses a **bead** of borax, produced by fusion on a platinum wire, is heated with a particle of the unknown compound and its color then examined. The colors are similar to those already described under colored glass (§ 451).

When hydrochloric or nitric acid is added to a hot, strong solution of borax, much of the boric acid crystallizes out when the mixture cools:

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3 \downarrow$$

A borate can be *recognized* by adding hydrochloric acid to the solution, dipping turmeric paper in the liquid, and drying it. The color is reddish brown and, when touched with caustic soda solution, becomes greenish black.

455. Exercises.

1. Make an equation for the preparation of, (a) lead silicate $PbSiO_3$ by fusion of litharge PbO and sand, (b) potassium silicate K_2SiO_3.

2. The inside surface of the bottle of sodium hydroxide solution becomes etched and dull. To what is this due?

3. What is the valence of boron?

4. Why is not all of the boric acid deposited from a hot solution containing it?

5. Write an equation for the effect of heat upon borax.

6. Why does the addition of borax render a glass more easily fusible?

CHAPTER XXIX.

COMPOUNDS OF SODIUM AND POTASSIUM.

456. We have already considered sodium and sodium hydroxide (Chap. XIII). In this chapter we take up the other important compounds of sodium and their uses, and we devote some space also to potassium and its more useful compounds.

In general, we shall find that these metals and their corresponding compounds are very much alike in properties. The chief differences are that the sodium compounds are usually cheaper, and that, on account of the difference in the atomic weights of the two elements (sodium 23, potassium 39), smaller weights of the sodium compounds suffice for a given use involving chemical interaction. For these reasons the sodium compound finds, in most cases, more applications.

Sodium and potassium are *univalent*, and both are *very active* as metallic elements. Their hydroxides being strongly alkaline, the elements are often called the *metals of the alkalies*.

SODIUM Na.

457. Sodium derives its symbol Na from its German name, *natrium*. All compounds of sodium, when heated with a Bunsen burner, confer a strong yellow tint upon the flame.

458. Occurrence. Sea water contains about 2.5 per cent of sodium chloride NaCl. The same compound is found in extensive deposits (rock salt) at Stassfurt and Reichenhall in Germany, in Cheshire (England), and in Michigan, Ohio, Kansas, and elsewhere in the United States. Sodium nitrate

(Chile saltpeter) occurs chiefly in an extensive bed on the border between Chile and Peru, from which almost our entire supply is at present obtained.

The preparation and properties of the metal are described elsewhere (pp. 119–121).

459. Sodium Chloride NaCl. This compound is obtained by allowing water to flow into the deposits of rock salt and then pumping the solution to the surface and evaporating the water. A certain amount is made, by evaporation, from sea water. The solution is first concentrated, either by solar evaporation in shallow pools or, in northern latitudes, by allowing such pools partially to freeze and then removing the ice.

The salt crystallizes in white cubes. It is a necessary article of diet. For example, it furnishes the hydrochloric acid required in digestion (p. 100). Its chief application, however, is in the manufacture of other compounds of sodium.

460. Sodium Bicarbonate $NaHCO_3$, Manufacture. This salt is manufactured by the interaction of sodium chloride and ammonium-hydrogen carbonate in the **Solvay** or **ammonia-soda process.** In the very concentrated solutions which are used, a great part of the sodium-hydrogen carbonate is precipitated:

$$NaCl + NH_4HCO_3 \rightleftarrows NaHCO_3 \downarrow + NH_4Cl. \qquad (1)$$

In practice salt is dissolved in water and the solution is saturated with ammonia gas. The mixture is placed in an iron tower filled with perforated shelves. Carbon dioxide, made by heating lime-stone in special kilns (p. 159), is forced in at the bottom. The perforations split up the gas into small bubbles, and facilitate its solution to form carbonic acid H_2CO_3. With the ammonium hydroxide NH_4OH in the liquid it gives ammonium-hydrogen carbonate:

$$NH_4OH + H_2CO_3 \rightarrow NH_4HCO_3 + H_2O. \qquad (2)$$

The product interacts as in equation (1). The sodium bicarbonate is precipitated and is freed from the liquor in filter presses or centrifugals. The ammonia is recovered for use by treating the residual liquor, containing ammonium chloride, with the quicklime CaO from the kilns. The quicklime, with the water, gives slaked lime $Ca(OH)_2$ and the latter liberates the ammonia (p. 201):

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_4OH \rightarrow 2NH_3 \uparrow + 2H_2O.$$

The waste liquor contains calcium chloride, and a considerable proportion of unused sodium chloride, along with an amount of sodium bicarbonate which is required to saturate it and is not recoverable.

461. Properties of Sodium Bicarbonate $NaHCO_3$. This salt is a fine, *white*, not obviously crystalline powder, which is only moderately *soluble* in water. It is commonly known as **baking soda.**

It *decomposes* slowly in an open vessel, even when cold. When heated, it rapidly gives off carbon dioxide and water, and leaves sodium carbonate:

Skeleton: $NaHCO_3 \rightleftarrows Na_2CO_3 + H_2CO_3 \rightleftarrows H_2O + CO_2$
Balanced: $2NaHCO_3 \rightleftarrows Na_2CO_3 + H_2O + CO_2$ (1)

Like all carbonates, when *treated with an acid,* it gives carbonic acid and this, in turn, gives water and carbon dioxide:

$$NaHCO_3 + HCl \rightleftarrows NaCl + H_2CO_3 \rightleftarrows H_2O + CO_2 \uparrow \quad (2)$$

This property leads to its use in fire extinguishers (p. 161).

462. Baking Powders. The purpose of the powder is to generate carbon dioxide in the dough. The bubbles of the gas are retained by the sticky gluten of the flour. They expand when the dough is baked, and give to it the open texture which, when the bread is eaten, facilitates access of the saliva to every particle.

Baking soda, if used alone, will give off, when heated, half the carbon dioxide it contains (equation (1), § 461). The sodium carbonate which remains in the bread, however, has an acrid taste. By its action on the gluten in the flour, it gives also a yellow color and an unpleasant odor. Finally, the carbonate of soda tends to neutralize the gastric juice (acid) of the stomach and so to interfere with digestion.

To obviate these difficulties sour milk (containing lactic acid) is sometimes used in making the dough. Occasionally vinegar (p. 186) is added. Most frequently a baking powder, containing an acid substance along with the soda, is employed. The acid substances contained in baking powders are alum, acid-phosphate of sodium, or potassium-hydrogen tartrate. The last, known commonly as **cream of tartar** $HKC_4H_4O_6$, is considered the most satisfactory:

$$HKC_4H_4O_6 + NaHCO_3 \rightarrow NaKC_4H_4O_6 + H_2CO_3 \rightarrow H_2O + CO_2.$$

The advantages of cream of tartar are, (1) that it is somewhat insoluble, and so, even when wet, it does not act upon the soda until ample time has been allowed for complete mixing with the dough, and (2) that the sodium-potassium tartrate (**Rochelle salt**) which remains is not known to be harmful.

It is important that the soda and cream of tartar should be used *in the correct proportions*, which can be calculated from the equation. In commercial baking powders a little cornflour is added, to keep the particles of the other compounds apart and prevent that gradual interaction which otherwise would be bound to occur.

463. Bakers' Bread. The "raising" of bakers' bread is effected by adding yeast. The batch is "set" in a warm place for some hours to permit the yeast to propagate and to act upon the sugar in the flour. In this action, as we have seen (p. 184), carbon dioxide and alcohol are produced. A little sugar, molasses, or malt extract is added to the dough, to afford a larger supply of the sugar required for the production of the carbon dioxide.

The whites of eggs "raise" cake, without the presence of any soda, because of the expansion under heat of the bubbles of air entangled with the albumen when the eggs are "whipped."

464. Sodium Carbonate Na_2CO_3. This salt is manufactured by heating sodium bicarbonate. It is made also by the **Le Blanc process.** Sodium chloride is treated at a red heat with an equivalent amount of sulphuric acid, giving sodium sulphate Na_2SO_4. The latter is roasted with powdered coal and limestone. The coal reduces the sulphate to sodium sulphide Na_2S, and the latter interacts with the limestone giving sodium carbonate and calcium sulphide CaS. The carbonate is separated by solution in water. The solution, when concentrated, gives crystals of the decahydrate, **washing soda** $Na_2CO_3, 10H_2O$. The latter, when heated, leaves " soda-ash " or " calcined soda " Na_2CO_3.

Sodium carbonate Na_2CO_3 is used in making sodium hydroxide (p. 121) and glass (p. 272), and to soften water (see § 534). As about two-thirds of washing soda is water, it is cheaper to ship the anhydrous form, except when the hydrate is wanted, as for washing.

465. Properties of Sodium Carbonate Solution. The solution is not neutral to litmus, as we might expect, but distinctly **alkaline.** The explanation is that water is ionized, although very slightly, and interacts with the carbonate to a minute extent:

$$Na_2CO_3 + H_2O \rightleftarrows NaOH + NaHCO_3.$$

The action produces a base and an acid-salt, and in so far is the reverse of neutralization (p. 129). An acid or acid-salt giving H^+, and a base giving OH^-, have opposite effects upon litmus. If they were equally ionized, and therefore *equally active,* they would leave the indicator unchanged. In this instance, however, the acid (carbonic acid) is a very feeble acid and hardly affects litmus, while the base (sodium hydroxide) is a very active base (p. 138). Hence, although there is but little of either substance formed, still the base is easily able to show its presence by turning red (or neutral) litmus blue.

466. Hydrolysis of Salts. This interaction of a salt with water is called **hydrolysis** (Greek, *decomposition by water,* p. 181). All salts are hydrolyzed, at least to a slight extent. This is no more than we should expect, for salts can be formed by an acid and a base giving, by double decomposition, a salt and water, and we have already asserted that double decompositions of ionogens *are all reversible. The effect is noticed,* however, chiefly *when the acid and base are of very unequal activity.* **A salt which, by hydrolysis, gives an active base and a weak acid, furnishes a solution the reaction of which is basic.** Thus, sodium chloride solution is neutral:

$$NaCl + H_2O \rightleftarrows NaOH + HCl$$

because the products of hydrolysis are both active. But sodium sulphide solution is alkaline:

$$Na_2S + H_2O \rightleftarrows NaOH + NaHS$$

because sodium-hydrogen sulphide HNaS is a very feeble acid.

Conversely, **if the salt gives, by hydrolysis, a weak base and an active acid, then the solution is acid in reaction.** Thus, the solution of cupric sulphate is acid:

$$CuSO_4 + 2H_2O \rightleftarrows Cu(OH)_2 + H_2SO_4$$

because cupric hydroxide is a feeble base.

467. Sodium Nitrate $NaNO_3$. This salt is prepared by recrystallizing Chile saltpeter (p. 240). When heated, it gives off oxygen, leaving **sodium nitrite** $NaNO_2$, a compound much used as a source of nitrous acid in the manufacture of organic dyestuffs.

Sodium nitrate is at present the chief source of nitric acid (p. 240). On account of its solubility (p. 265) and its nitrogen content, it is valuable as a fertilizer. It is used also in the manufacture of cheap grades of gunpowder. Much of it is converted into potassium nitrate, as this salt is less hygroscopic, and the gunpowder made from it keeps better.

468. Other Salts of Sodium. Several of them, such as the **peroxide** (p. 229), the **silicate** (p. 272), and the **tetraborate** (p. 275), have been described already. Sodium **sulphate** Na_2SO_4 (p. 281) is used as a substitute for sodium carbonate in making cheap glass. Sodium **sulphite** Na_2SO_3 (p. 221), made by the action of sulphur dioxide on an aqueous solution of sodium hydroxide, is a convenient source of sulphur dioxide and is also used as a preservative. Sodium **thiosulphate** $Na_2S_2O_3$ (" hypo ") can be obtained readily by boiling sodium sulphite solution with sulphur:

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

and is used in fixing photographs. Sodium **cyanide** NaNC (preparation, see § 536) is used in extracting gold from its ores (Chap. XL).

POTASSIUM K.

469. Potassium receives its symbol from the initial of the German word for it, *kalium* (related to the word *alkali*). All compounds of potassium confer a violet color upon the Bunsen flame.

470. Occurrence. Certain deposits of rock salt, especially those at Stassfurt, are covered by a layer of other salts, of which **potassium chloride** KCl (sylvite) forms a large part.

The soil in India and other tropical countries contains potassium nitrate, the nitrogen for which is derived from the decomposition of animal refuse. The nitrogen is oxidized by the help of certain bacteria to nitric acid, and the latter interacts with compounds of potassium in the soil. In the Southern States, during the Civil War, the supply of imported niter was cut off and potassium nitrate for gunpowder was cultivated successfully in this way.

Felspar $KAlSi_3O_8$ is a common constituent of many rocks, such as granite. When such rock material, contained in the soil, is decomposed by weathering, the felspar gives clay $HAlSiO_4$ and soluble compounds of potassium. The latter afford an indispensable item in the diet of plants. There are immense quantities of felspar available, but the process of weathering is very slow, and in many agricultural regions the soil is therefore deficient in available potash. An economical process for manufacturing compounds of potassium from felspar is now being sought.

The giant seaweeds of the Pacific coast have been found to take up from the sea water, and finally to yield in their ash, an unusually large proportion of salts of potassium. Until some suitable source has been brought into use, however, the world will remain dependent upon the Stassfurt deposits for the greater part of the potassium it requires for fertilizers, gunpowder, and a number of other products.

471. Potassium. The metal is prepared from potassium hydroxide by the same apparatus used in making sodium (p. 119). Its properties are similar to those of sodium, excepting that it is more active (p. 120). It has no uses.

472. Potassium Chloride KCl. This is a white salt, found at Stassfurt. It is the chief source of other compounds of potassium.

473. Potassium Carbonate K_2CO_3, Preparation. The water used in scouring wool leaves, when evaporated, the potassium salts of organic acids. When the residue is roasted, potassium carbonate remains. Again, as we have seen, plants absorb potassium compounds from the soil. Hence, wood ashes contain considerable amounts of potassium carbonate, and were indeed originally the only source of this compound. The sugar beet takes up exceptional quantities of potassium and, after all the sugar has been removed from the extract, potassium carbonate is obtained by evaporating the liquid and calcining the residue. Much of the salt is also manufactured direct from potassium chloride.

474. Properties of Potassium Carbonate. This salt, being much more soluble than sodium carbonate, is deliquescent. Its aqueous solution is alkaline in reaction. It is used in making soft soap (§ 498) and difficultly fusible glass (p. 273).

475. Potassium Bicarbonate $KHCO_3$. When carbon dioxide is led into potassium carbonate solution, **potassium bicarbonate** $KHCO_3$ is formed:

$$CO_2 + H_2O \rightleftarrows H_2CO_3 + K_2CO_3 \rightleftarrows 2KHCO_3.$$

The bicarbonate decomposes easily, especially when warmed, reversing the above action (read the equation backwards). This occurs even in the solution. Hence carbon dioxide can be forced *by pressure* in large amounts into a warm solution of potassium carbonate, and liberated again by pumping so as to create a vacuum. This plan is used as a means of purifying carbon dioxide (p. 159). The same quantity of potassium carbonate can be used over and over again.

Before the nineteenth century, when potassium salts were cheaper than sodium salts, potassium bicarbonate made from wood ashes was used in raising bread. It was known as **saleratus** (Latin, *aerated salt*) — a name which is now sometimes given to the baking soda which has displaced it.

476. Potassium Hydroxide KOH. This alkali is made like sodium hydroxide (p. 121). Either potassium carbonate is treated with slaked lime, or potassium chloride is electrolyzed in a Castner (p. 121) or in a Townsend or a Briggs cell. The solution is evaporated, and the substance cast in slender sticks.

Its properties are much like those of sodium hydroxide. It is used in making soft soap and other compounds of potassium.

477. Potassium Nitrate KNO_3. The supply of the natural nitrate being insufficient, the salt is made by double decomposition from the Chile saltpeter $NaNO_3$

$$NaNO_3 + KCl \rightarrow KNO_3 + NaCl \downarrow$$

Sodium chloride is not much more soluble in hot water than in cold. The three other salts, however, become very soluble as the temperature rises. Hence, when sodium nitrate and potassium chloride are heated with very little water, they dissolve, sodium chloride is precipitated, and potassium nitrate remains in solution. The mass is filtered quickly through canvas to separate the precipitate, and potassium nitrate crystallizes from the filtrate as it cools.

The salt is used in making gunpowder and fireworks. It is employed also in preserving ham and corned beef.

478. Gunpowder. Gunpowder is composed of potassium nitrate (75 per cent), charcoal (15 per cent), and sulphur (10 per cent). The ingredients are moistened with water, and intimately mixed by grinding under the heavy rollers of a mill. The "mill cake" is then broken up and granulated to the required size.

The explosion results largely in the union of the charcoal with the oxygen from the nitrate and of the sulphur with the potassium:

$$16KNO_3 + 21C + 5S \rightarrow 5K_2CO_3 + K_2SO_4 + 2K_2S_2 + 13CO_2 + 3CO + 8N_2.$$

One gram of powder yields 264 c.c. of gas (CO_2, CO, and N_2) measured at 0° and 760 mm., and a much larger volume at the temperature of the explosion. One gram produces about 660 calories of heat. The *explosion* is due to the *suddenness* with which the gases are generated and the heat is developed. The smoke is composed of particles of the three solid compounds of potassium and is therefore very slow in dissipating itself. Smokeless powder (§§511–513) produces no solids when it explodes.

Gunpowder is still used in mining, and for detonating charges of smokeless powder.

479. Other Compounds of Potassium. Potassium **bromide** KBr (p. 254), used in medicine to relieve nervousness and to produce sleep, potassium **iodide** KI (p. 257), used also in medicine, and potassium **chlorate** $KClO_3$ (p. 264), employed in making matches and fireworks, have already been mentioned. Potassium **sulphate** K_2SO_4, made by the action of sulphuric acid upon potassium chloride at a red heat, is employed in making alum (§ 561).

480. Exercises.

1. What two methods are used for concentrating a solution (p. 278)? Explain why each is effective.

2. In the Solvay process why is the ammonia dissolved in the salt solution, and not separately in water? Make the equation for the action of heat on limestone.

3. (a) In what proportions by weight should baking soda and cream of tartar be used in raising bread? (b) What is the objection to using

too large a proportion of baking soda? (c) Why must baking powder be kept in a dry, cool place?

4. Why does vinegar liberate carbon dioxide from baking soda? Make the equation for the action.

5. In what way must the moisture in the dough contribute to the raising of bread or cake in the oven?

6. Make the equations for the action of: (a) coal (carbon) on sodium sulphate, (b) sulphuric acid upon sodium carbonate.

7. What is the exact percentage of water in washing soda?

8. What will be the reactions to litmus of aqueous solutions of: (a) borax, (b) sodium bromide, (c) sodium silicate, (d) sodium peroxide, (e) sodium nitrate?

9. Why does a piece of glass, when strongly heated, confer a yellow color on the Bunsen flame?

CHAPTER XXX.

THE RECOGNITION OF SUBSTANCES, I — A REVIEW OF THE NON-METALLIC ELEMENTS.

481. In the chapters preceding we have classified our substances under one of the *chemical* elements they contained. Thus, starch, sugar, and alcohol were put under carbon. Hydrogen sulphide and sulphuric acid were considered as compounds of sulphur. Now this classification is of a *theoretical* nature. That starch, sugar, and alcohol all contain carbon can not be told by mere *inspection*. We have to make experiments, and to reason about the results, before we reach this inference. Thus we put our *inference* as the title of the chapter, and distributed the observations and data through it. There is, however, another way of classifying the facts, which is just the opposite of this one. It is the *practical* classification. When we obtain a specimen, or when a substance appears in the course of an experiment, we must be able to tell what particular substance it is. If it is a white powder, it may contain almost any of the whole list of elements. It may be any one of several thousands of substances. We can recognize it only by its physical properties (p. 3) and by the physical properties of other substances that we can get from it by interaction with known chemical compounds. We need, therefore, a plan of operation, and this plan must be based upon a *classification by physical properties*, not by constituents.

One benefit of the discussion of such a plan is that it will afford us a *review* of some of the facts already mentioned, by presenting the same facts from a different view-point, and by showing the uses to which they may be put. To avoid unnecessary repetition, we shall refer frequently to the previous statements of the facts. To understand what is here said, therefore, the reader should look up every reference and reread the statement.

482. Is the Material a Mixture? The first question that occurs to us is, whether the material is a single substance or a mixture. When it is a mixture, we can often, though not always, very quickly find this out.

If it is **a solid mass or powder,** we examine it with the naked *eye* and with the help of a *lens.* If we see two or more kinds of particles, as in granite (p. 4), in a mixture of sand and sugar, or in a piece of rusty iron, the kinds differing in form or color or both, then it probably is a mixture.

Whether it appears to the eye to be a mixture, or not, we can next try a *solvent,* such as water, ether, or carbon tetrachloride. If a part of a small sample refuses to dissolve (*e.g.* sand), while the rest dissolves (*e.g.* sugar), we have shown that there are two different sets of physical properties, and therefore two different substances (p. 5) present. As there may be very little of the soluble substance in the mixture, we may not perceive at once that anything has dissolved. So we allow a drop of the liquid to evaporate on a clean watch crystal, and observe whether any residue remains.

Again, a *magnetized* knife blade may pick out certain particles (*e.g.* iron) and not others.

If the material is **a liquid,** we depend largely on differences in the *volatility* of different substances to find out whether it is a mixture. If a drop evaporates on a watch glass, leaving a residue (solid or liquid) which does not evaporate, then it is a mixture. If this test fails, because all, or none, evaporates, then we must distil the liquid, with the bulb and most of the stem of a thermometer in the vapor (Fig. 28, p. 54), and note whether the whole comes over at one temperature (single substance, in most cases) or whether the temperature changes as the distillation proceeds (mixture, such as petroleum, pp. 168–170).

These are simply a few examples intended to show how, when a practical problem is before us for solution, we use *physical properties* as the basis of our reasoning and classification.

483. The Recognition of a Single Substance. The majority of the substances we have met with are acids, bases, or salts. In identifying a substance of one of these classes, it is convenient to attempt the recognition of the positive and of the negative radicals (or ions) as *two almost separate problems.* In other words, we investigate one radical at a time. On the other hand, substances which do not belong to any of these classes, such as simple substances (sulphur, carbon, chlorine, etc.), oxides (sulphur dioxide, carbon monoxide, etc.), and many organic substances (*e.g.* carbon disulphide), are investigated as a single problem.

484. Scope of This Chapter. In discussing the recognition of a single substance we shall, for the present, limit ourselves to the non-metallic elements. We shall consider the elementary substances themselves (sulphur, oxygen, etc.), the oxides of such elements, the few organic compounds described, the non-metallic negative ions, and ammonium-ion. We shall leave out of consideration until later (Chap. XLII) the metallic elements (including As, Sb, Bi, Na and K). We shall also ignore the metallic positive radicals, although one of these (or hydrogen-ion) must inevitably be combined with the negative radical under consideration.

485. External Examination (Solids). The specimen may be a solid, a liquid, or a gas. We should note in which of these STATES it exists under room conditions. What follows applies only to SOLIDS — the liquids and gases will be taken up later (§§ 489, 490).

Without training in crystallography we can tell little about the CRYSTALLINE FORM (p. 88) of the specimen. But anything conspicuous, such as **needle-shape** or **cubical** formation of the particles, must be noted.

The COLOR, if any, is significant. If **yellow**, the specimen may be *sulphur* (p. 208), if **black**, *carbon* (amorphous or graphite, p. 149), if **black** and crystalline, with **violet** vapor, *iodine* (p. 255). Most substances are colorless.

The ODOR, if any, must be noted. Many salts of ammonium (carbonate, sulphide, etc.) smell of *ammonia* (p. 202). Some sulphides (of sodium, potassium, ammonium, etc.) smell of *hydrogen sulphide* (p. 213). Some acetates smell of *acetic acid* and hypochlorites of *hypochlorous acid* (p. 235).* Some chlorides (*e.g.* PCl_5 and $AlCl_3$), in moist air, give *hydrogen chloride*, with the odor and fumes characteristic of that substance.

486. Effect of Heating (Solids). A great deal may be learned by heating as much of the specimen as will fill the rounded bottom of a small, dry test-tube (Fig. 76).

Fig. 76

The substance may FUSE. Many substances, such as some chlorides and most hydrates, do so. Continue heating.

A SUBLIMATE (solid deposit on the cold part of the tube) may appear. **Black** crystals (from violet vapor) are *iodine;* **white** crystals, with the limitations we have set, show the substance to be a *salt of ammonium* (p. 205). Confirm by smelling, and by adding sodium hydroxide (better than slaked lime) to the original substance (p. 201). (Salts of mercury sublime also.)

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* Many experimental details, essential for the successful performance by a beginner of the tests described in this chapter are here omitted. They will be found in the Author's *Laboratory Outline of Elementary Chemistry.*

A **REDDISH-BROWN LIQUID** condenses, becoming, when cold, a yellow solid. The substance was *sulphur* or a *sulphide* (such as FeS_2, p. 208).

WATER condenses. *Hydrates, acid salts,* and some *organic* compounds decompose to give water. Test the water with litmus paper. An **acid** reaction indicates an *acid salt* (§ 461), an easily hydrolyzed salt (*e.g.* $FeCl_3, 6H_2O$) or *organic acid.* Continue heating, inclining the tube mouth downwards, removing condensed water with filter paper until no more comes off, and then heat the residue.

A **GAS** is given off. The gas may be **violet** (some *iodides*) or **brown** (some *nitrates,* § 394, and some *bromides*). If brown, lower a glass rod dipped in silver nitrate solution into the gas in the tube. Bromine will give a white precipitate (AgBr). In case of a negative result try the test for nitrates (p. 245).

The gas may be **colorless.** If it has an **odor,** it may be ammonia from a *salt* of *ammonium,* sulphur dioxide from a *bisulphite* (p. 221, decomposes as in § 461) or from oxidation of a *sulphide* (p. 218). A stifling odor with **fumes** may be sulphur trioxide from some *sulphates* (*e.g.* ferric sulphate), or decomposition products from some *organic* matters.

The gas is **colorless** and **odorless.** It may be oxygen (test with long, glowing splinter of wood) from a *peroxide, chlorate, perchlorate,* or *nitrate* (of K or Na). To learn which of these it is, dissolve or suspend a little of the substance in water, add dilute sulphuric acid, and test for hydrogen peroxide (p. 231). In case of a negative result examine the residue as in § 488. Nitrous oxide also relights the splinter. In this case the substance was *ammonium nitrate* (p. 248) and can be vaporized completely, leaving no residue.

A **colorless, odorless** gas may be carbon dioxide, coming from a *bicarbonate* or a *carbonate* (except of K or Na). Lower a glass rod dipped in lime-water into the gas in the test-tube (white precipitate, $CaCO_3 \downarrow$, p. 161).

The substance CARBONIZES OR CHARS and gives an odor of smoldering wood or burning flesh. The compound is *organic*. Identify, by properties, starch (p. 179), glucose (p. 180), sucrose (p. 182).

Heating may produce NO EFFECT. On the other hand, *more than one* of these effects (*e.g.* both water and sulphur dioxide from a bisulphite) may be given by the same specimens.

If heating produces any effect, continue heating until all change ceases, and preserve the residue for use in § 488.

In most cases other distinctive properties will be found on the pages referred to.

487. Effect of Sulphuric Acid on Solids. Fill the rounded bottom (only) of a test-tube with the substance,* add just enough concentrated sulphuric acid to moisten the sample, and warm slightly.

A GAS (effervescence) WHICH FUMES in the breath may be given off. If the gas is **brown** or **yellow,** it may be bromine (bleaches litmus paper) mixed with hydrogen bromide from a bromide (p. 253). If **violet,** with brown deposit, accompanied by an **odor** of hydrogen sulphide, it is iodine from an *iodide* (p. 256).

If the gas fumes, but is **colorless,** it may be hydrogen chloride from a *chloride* (add manganese dioxide to get chlorine, pp. 108–109). It may be hydrogen fluoride from a *fluoride* (a moistened glass rod acquires white precipitate of silicic acid, p. 272). It may be nitric acid from a *nitrate* (when cold, add to a little water and copper, p. 245).

The gas DOES NOT FUME. If **yellow** it may be chlorine dioxide from a *chlorate* or chlorine from *bleaching powder* (p. 234) or nitrous anhydride from a *nitrite* (p. 248).

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* In case the substance gave oxygen in § 486, use only a few particles, at first, to find out whether it is a chlorate (ClO_2 is explosive).

The gas does not fume and is **colorless.** An **odor** of **sulphur dioxide** indicates a *sulphite* (p. 219) or *sulphide* (p. 225, par. 4). An **odor of hydrogen sulphide** indicates a *sulphide.* If the gas is odorless, it may be carbon monoxide (burns, leaving carbon dioxide) from a formate (p. 162), or oxygen from some *oxides* or a *peroxide,* or carbon dioxide from a carbonate.

NO GAS evolved indicates a *silicate, sulphate* (test, p. 224), *phosphate* (test, p. 265), or a basic *oxide.*

488. Sulphuric Acid on the Residue from § 486. If the substance gave off oxygen when heated alone (§ 486), add a drop or two of concentrated sulphuric acid. If the specimen now gives a yellow gas (nitrous anhydride), the original substance was a *nitrate* (of K or Na), from which the nitrite was formed by heating (p. 245). If it gives a **colorless, fuming** gas (HCl), the original substance was a chlorate or perchlorate (p. 79).

489. Examination of a Liquid. Test the specimen with LITMUS PAPER. **A marked acid reaction** may be due to an *acid,* such as concentrated or dilute sulphuric acid (pp. 224–5), concentrated (p. 241) or dilute nitric acid (p. 244), concentrated (p. 96) or dilute hydrochloric acid (p. 97), hydrobromic acid (p. 254), hydriodic acid (p. 256), phosphoric acid (p. 264), sulphurous acid (p. 220), or an organic acid; also an acid-salt (p. 139), or a hydrolyzed salt (p. 282).

If it **bleaches** litmus paper, it may be *chlorine-water* or *bromine-water* (odor).

If it is markedly **alkaline** in reaction, it may be a solution of a *base* (NaOH, KOH, NH_4OH, etc.) or a hydrolyzed *salt* (p. 282).

Note the ODOR. Ammonium hydroxide, hydrogen sulphide solution, sulphurous acid, concentrated nitric acid and concentrated halide acids all have odors. Alcohol, acetic acid, carbon disulphide, carbon tetrachloride, and hydrocarbons (*e.g.* gasoline) have odors easily distinguished from those of the foregoing.

EVAPORATE A FEW DROPS TO DRYNESS on a watch crystal. A solid (or liquid) residue shows that the original substance was a *solution* in water (or possibly alcohol or some other solvent, if the vapor has an odor indicating this). If there is a solid residue, a quantity of it may be obtained by evaporating a larger amount of the liquid, and may then be treated as a solid (§§ 485–488).

If the specimen leaves **no residue,** and is not acid or alkaline but has an **odor,** it may be one of the volatile organic compounds named above. If it is **odorless,** it may be a solution of hydrogen peroxide (p. 231) or simply pure water.

490. Examination of a Gas. The gas has a COLOR. A **brown** gas may be *bromine* or *nitrogen tetroxide*. The former liberates iodine from potassium iodide solution (p. 256), but not bromine from a bromide (insert rods moistened with solutions of an iodide and a bromide). The latter gas becomes deeper brown on warming (p. 246). A **greenish-yellow** gas is *chlorine*. It bleaches, and displaces bromine from a solution of a bromide (p. 254).

The gas may BECOME COLORED (yellow or brown) on admitting air. It is *nitric oxide* (p. 245).

The gas may have a distinctive ODOR. *Sulphur dioxide, hydrogen sulphide,* and *ammonia,* also *ozone,* are of this kind.

The gas may FUME in the breath. The *chloride, bromide,* and *iodide* of *hydrogen* do so. Distinguish by dissolving in little water and adding manganese dioxide (pp. 109, 252, 255).

The gas may be COMBUSTIBLE. Burning with a **blue flame** indicates *hydrogen* (vessel bedewed with moisture), or carbon *monoxide* (leaving carbon dioxide, test p. 293). Burning with a slightly **luminous flame** indicates *methane* (p. 272) and a very luminous flame (often depositing carbon) indicates *ethylene* (p. 169) or *acetylene* (p. 171).

The gas may RELIGHT A GLOWING SPLINTER OF WOOD. This is *oxygen*, *ozone* (odor), or *nitrous oxide* (p. 248). The first two, with nitric oxide, give a brown gas (p. 245), the last does not. The test with a glowing splinter of wood works with *pure* oxygen only: the test with nitric oxide will show the presence of even a little oxygen in a mixture.

The gas having NONE of these properties is *nitrogen* (p. 190).

In most cases other distinctive properties will be found on the pages referred to.

491. Exercises.

1. Look up the references, and give the properties (physical as well as chemical), other than those mentioned in § 485, by which you should recognize: (a) sulphur, (b) carbon, and (c) iodine.

2. Same question in regard to (§ 485): (a) ammonia, (b) hydrogen sulphide, and (c) hypochlorous acid.

3. Same question in regard to (§ 486): (a) an acid salt, (b) a hydrate, (c) nitrogen peroxide, (d) bromine, (e) sulphur trioxide, (f) hydrogen peroxide, (g) ammonium nitrate, (h) carbon dioxide, (i) starch, (j) glucose, and (k) sucrose.

4. Same question in regard to (§ 487): (a) a bromide, (b) an iodide, (c) a nitrate, (d) bleaching powder, (e) sulphur dioxide, (f) carbon monoxide, (g) a silicate, (h) a sulphate, and (i) a phosphate.

5. Same question in regard to (§ 488) a nitrite.

6. Same question in regard to (§ 489): (a) conc. and (b) dil. sulphuric acid, (c) conc. and (d) dil. nitric acid, (e) conc. and (f) dil. hydrochloric acid, (g) hydrobromic acid, (h) hydriodic acid, (i) phosphoric acid, (j) sulphurous acid.

7. Same question in regard to (§ 489): (a) chlorine-water, (b) alcohol, (c) acetic acid, (d) carbon disulphide, (e) carbon tetrachloride, (f) a hydrocarbon.

8. Same question in regard to (§ 490): (a) nitric oxide, (b) hydrogen, (c) methane, (d) ethylene, (e) acetylene, (f) nitrous oxide, (g) ozone, (h) nitrogen.

CHAPTER XXXI.

FATS, SOAPS, AND RELATED COMPOUNDS.

492. Thus far we have mentioned only one organic acid, namely acetic acid HCO_2CH_3 (p. 186) which is manufactured by the oxidation of ethyl alcohol. But many such acids are known and, as we might expect, their composition places them in series just like the hydrocarbon series.

493. Organic Acids and their Salts. The general formula of the main (saturated) series is $H(CO_2C_nH_{2n+1})$. Thus:

For $n = 0$, $H(CO_2H)$ Formic acid.
$n = 1$, $H(CO_2CH_3)$ Acetic acid.
$n = 3$, $H(CO_2C_3H_7)$ Butyric acid.
$n = 15$, $H(CO_2C_{15}H_{31})$ Palmitic acid.
$n = 17$, $H(CO_2C_{17}H_{35})$ Stearic acid.

Those containing less hydrogen are unsaturated:

$n = 17$, $H(CO_2C_{17}H_{33})$ Oleic acid.

Formic, acetic and butyric acids are liquids. Palmitic and stearic acids are solid. Oleic acid is a liquid.

These are all monobasic acids. Those with large molecular weights are insoluble in water. All the acids react with sodium hydroxide solution, however, giving sodium salts. Thus stearic acid gives sodium stearate:

$$NaOH + H(CO_2C_{17}H_{35}) \rightarrow H_2O + Na(CO_2C_{17}H_{35}).$$

Some other salts are: $NaCO_2H$ sodium formate, $NaCO_2CH_3$ acetate of sodium, $Na(CO_2C_{15}H_{31})$ palmitate of sodium,

$Na(CO_2C_{17}H_{33})$ sodium oleate. Those salts are all soluble in water and *common soap* is a mixture of the last two with sodium stearate. On account of their extensive use in the laundry, and for other purposes in the household, it is very important that we should gain a knowledge of the modes of manufacture and of the properties of these salts. To accomplish this we must first learn the nature of fat, from which soap is made.

494. Abbreviated Formulæ. In discussing these substances it will sometimes be convenient to abbreviate the formulæ, so that a fatty acid is represented by HCO_2R and a salt by $NaCO_2R$ or $Ca(CO_2R)_2$. Here R stands for a hydrocarbon radical or group of atoms, such as C_nH_{2n+1}.

495. Esters. If we mix alcohol and acetic acid, no immediate action takes place. But, *after some days or weeks,* we begin to notice a fragrant odor due to the formation of **ethyl acetate** $C_2H_5(CO_2CH_3)$:

$$C_2H_5OH + H(CO_2CH_3) \rightarrow C_2H_5(CO_2CH_3) + H_2O.$$

Addition of a little sulphuric acid and warming hastens the action, and the odor becomes evident in a few minutes.

The foregoing action, when stated in an equation, looks like a neutralization (p. 129). But it differs sharply from ordinary neutralization in several respects. The alcohol is not a base in its properties, although in mere formula or composition it resembles one. In aqueous solution it does not conduct electricity or show the other properties of a base (p. 138). True neutralization takes place *instantaneously,* while the foregoing action, and all like it, proceed very slowly. Thus, although acetic acid is a true acid, it is not *here* interacting with a base.

Similar actions take place between any alcohol and any acid (organic or inorganic). Thus:

$$\underset{\text{amyl alcohol}}{C_5H_{11}OH} + \underset{\text{acetic acid}}{H(CO_2CH_3)} \rightarrow \underset{\substack{\text{amyl acetate}\\ \text{(banana oil)}}}{C_5H_{11}(CO_2CH_3)} + H_2O$$

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{acetic acid}}{3H(CO_2CH_3)} \rightarrow \underset{\text{glyceryl acetate}}{C_3H_5(CO_2CH_3)_3} + 3H_2O$$

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{palmitic acid}}{3H(CO_2C_{15}H_{31})} \rightarrow \underset{\substack{\text{glyceryl palmitate}\\ \text{(palmitin)}}}{C_3H_5(CO_2C_{15}H_{31})_3} + 3H_2O$$

The glyceryl radical $C_3H_5^{III}$ is trivalent, as the equations show. The actions into which it enters are, therefore, similar in form to those in which an hydroxide of a trivalent metal, such as aluminium, is acted upon by an acid:

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O.$$

The products of such actions are named as if they were salts, amyl acetate, etc., but they do not possess the properties of salts. They are not ionized in aqueous solution. To distinguish them from salts they are called **esters** — $R'(CO_2R)$.

496. Fats and Oils. Now the fats and oils found in the bodies of animals, or pressed from the seeds of plants, are composed mainly of various esters. Thus, **beef suet** is a mixture of about three-fourths glyceryl palmitate (palmitin) $C_3H_5(CO_2C_{15}H_{31})_3$, and glyceryl stearate (stearin) $C_3H_5(CO_2C_{17}H_{35})_3$, and one-fourth glyceryl oleate (olein) $C_3H_5(CO_2C_{17}H_{33})_3$. **Hog lard** contains about 40 per cent of the former and 60 per cent of the latter, and is therefore softer. **Butter** includes the same esters, with about 14 per cent of water. When butter is dried, the remaining fat contains about 8 per cent of glyceryl butyrate (butyrin) $C_3H_5(CO_2C_3H_7)_3$. **Olive oil** contains 75 per cent of olein. **Cotton seed oil** is similar in nature, and is used as a substitute for olive oil or for butter in cooking.

All the fats and oils contain, however, a small amount of the *free acids*, a fact of which we shall later learn the consequences (§ 508).

Oleomargarine is an artificial butter. It is made by straining melted beef fat and allowing it to stand at 24°. Much of the stearin crystallizes out and the remaining liquid (the "oleomargarine") is pressed out and allowed to solidify. The solid is finally mixed with a little of some oil, to render it softer, and is churned with milk to impart the proper flavor. Although it lacks the butyrin, the product is similar in chemical nature to butter, and is just as nutritious and wholesome.

Many **flavors, essences** and **perfumes** are mixtures of esters. Thus the flavor of pineapples is due largely to ethyl butyrate $C_2H_5(CO_2C_3H_7)$.

The fats and oils obtained from animals and plants are thus composed chiefly of esters. They must not be confused with *mineral* oils like petroleum, which are mixtures of hydrocarbons.

497. Physical Properties and Uses of the Fats and Oils. The fats and oils are all insoluble in water. Those with large molecular weights are also practically insoluble in cold alcohol. They are soluble, however, in ether, carbon disulphide, and carbon tetrachloride. Hence "grease spots" are not removed by water or alcohol, but are removed by rubbing with the other solvents. Benzine also dissolves fats, and hence is used in washing (**dry cleaning**) clothing made of silk or woolen materials.

The fats and oils belonging to the class of esters are nutritious, and a certain proportion of them is included in a healthy diet (see § 585). Large quantities of the same fats and oils are also used to make soap.

498. Chemical Properties of Fats and Oils. The chief chemical property of the fats and oils, and in fact of all esters, is that each can be *decomposed by water* to give the alcohol and acid from which (p. 300) it is derived. Thus, when ethyl acetate is boiled with water, it is slowly decomposed into ethyl alcohol and acetic acid:

$$C_2H_5(CO_2CH_3) + H_2O \rightarrow C_2H_5OH + HCO_2CH_3.$$

In the case of the fats and oils, they are heated in a closed vessel so as to secure a high temperature (about 200°):

$$\underset{\text{palmitin}}{C_3H_3(CO_2C_{15}H_{31})_3} + 3H_2O \rightarrow \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{palmitic acid}}{3HCO_2C_{15}H_{31}}.$$

When the mixture has cooled, the acid, which is insoluble in water, forms a solid cake, while the glycerine is dissolved in the water.

When tallow (beef fat) is treated in this way, the solid is a mixture of palmitic, stearic, and oleic acids. The latter, being liquid, is pressed out, and the solid material is used with paraffin in making candles (p. 170). The glycerine is separated from the water and used in making nitroglycerine and in medicine.

When the fat is heated with a solution of *caustic soda* NaOH, instead of water, *the sodium salts of the acids are obtained.* These sodium salts are known as *soaps* (see next paragraph), and the operation is called **saponification**:

$$\underset{\text{palmitin}}{C_3H_5(CO_2C_{15}H_{31})_3} + 3NaOH \rightarrow \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\substack{\text{sodium palmitate}\\\text{(a soap)}}}{3Na(CO_2C_{15}H_{31})}$$

The sodium palmitate, or other soap, is soluble in the water. When common salt is added, however, the soap coagulates and separates into a floating layer which solidifies on cooling.

Soft soap is made with potassium hydroxide, and is composed of the potassium salts of the organic acids.

499. Manufacture of Soap. Soap is made in large copper caldrons. These contain closed steam coils for heating, and pipes delivering live steam, when needed, for stirring the mass. The fat is mixed with caustic soda solution containing, at first, only about one-fourth of the total amount of the base that the above equation requires. When, after heating and stirring, a uniform mixture has been produced, the rest of the alkali is added gradually and the heating is continued until the reaction appears to be complete. Salt is now dissolved in the mixture and the soap separates as a curd. The curd floats, leaving the "spent lye," containing the salt solution and much of the glycerine, in the lower layer. This process is called **salting out.**

When the process stops at this point, the upper layer is known as **curd soap,** and may be dipped out and allowed to cool and solidify. Most "Marseilles" soaps are curd soaps made in this way. A large part of the imported "Castile" soaps are of the same kind.

Curd soaps contain salt, glycerine, adhering lye, and other impurities. To prepare a purer soap, the spent lye is run off, dilute brine is added to the soap, and the curd and brine are stirred up. When separation has again occurred, the brine is run off and the process repeated. Finally, some water is added, and steam is run in until the curd mixes completely with the water. When the solution stands, it "settles," that is, resolves itself once more into two distinct layers. The upper layer is called **settled soap.** The washing with brine and temporary dissolving in water remove the impurities, and hence settled soap is the purest variety. The greater part of the soap made in the United States and in Great Britain, and much of that made in other countries, is of this kind.

The qualities of soaps are varied by adding "fillers," such as sodium carbonate, borax, or sodium silicate. **Soap powders** are often made of ground soap mixed with sodium carbonate. Dyes and perfumes are sometimes added to soaps. Air bubbles are mixed with the soap, by beating, to give the floating varieties. Soap for scouring contains fine sand. Transparent soaps are made by dissolving the soap in alcohol, or by the addition of glycerine or sugar.

500. Chemical Properties of Soaps. The soaps, being sodium salts, dissolve in water and have the *usual properties of salts*. Thus, when an acid is added, double decomposition takes place:

$$\underset{\text{sodium palmitate}}{Na(CO_2C_{15}H_{31})} + HCl \rightarrow NaCl + \underset{\text{palmitic acid}}{H(CO_2C_{15}H_{31})} \downarrow$$

The *acids*, being insoluble, are thrown down as white precipitates.

When other salts are added, similar actions occur. Thus with calcium chloride solution, calcium palmitate is formed, and being insoluble, is precipitated:

$$2Na(CO_2C_{15}H_{31}) + CaCl_2 \rightarrow 2NaCl + Ca(CO_2C_{15}H_{31})_2 \downarrow$$

This action is important in connection with "hardness" in water (§ 532).

501. Colloidal Suspension. We have seen (p. 180) that starch can be suspended in water in such a fine state of division that the liquid is transparent, and *runs through a filter* without leaving any solid on the paper. Yet this "suspension" lacks some of the characteristic properties of a solution.

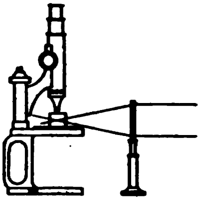

Fig. 77

The simplest proof, that this is a case of imitation solution, and not of true solution, is obtained by examining the liquid with the **ultra-microscope.** A converging beam of strong light is sent through the liquid *horizontally* (Fig. 77), and the illuminated place is viewed *from above*

JEAN PERRIN

French physical chemist. Investigator of the Brownian movement, 1870–

through a microscope. When the room is dark, and the only light comes from the horizontal beam, a colloidal solution shows minute points of light. A true solution — such as one of common salt or of sugar — remains perfectly dark. The points of light are produced by myriads of *minute suspended particles.* Solutions of soap, gelatine, and many dyes, blood serum, and innumerable other liquids contain such suspended particles.

The particles of a colloid (like starch), when viewed in this way, show a continual trembling or vibrating movement (Brownian movement), which is more distinct the smaller the particles, and is due to the impacts of the molecules of the solvent. Colloidal solutions of metals (gold, silver, platinum) can be made with particles so fine that they are of almost molecular dimensions, and shoot about, rapidly, rebounding sharply from the molecules they encounter.

502. Properties of Colloidal Suspensions. Suspended colloids differ from dissolved matter in several respects. Typical colloids are *not retained by filter paper.* The suspended matter does *not settle,* and it does *not diffuse* into a layer of the pure solvent.

When a solution of a colloid is placed in a " diffusion-shell " (test-tube shaped) of parchment, surrounded by pure water, *none of the colloid escapes* through the minute pores of the shell. Ordinary, non-colloidal solutes do escape, more or less rapidly according as the mass of their molecules is small or large (salt rapidly, sugar slowly). In this way a *mixture of colloid and non-colloid* (say, starch and salt) *can be separated,* if the water surrounding the shell is replaced by pure water at intervals until all the non-colloid has been removed. This method of separation is called **dialysis.**

Finally, matter in colloidal suspension can be *coagulated* (or flocculated), *and is then precipitated.*

503. Colloidal Matter in Soap Solutions. Explanation of Salting Out. Soaps are somewhat hydrolyzed in solution. Letting R (p. 299) stand for the hydrocarbon part of the acid radical:

$$Na(CO_2R) + H_2O \rightleftarrows H(CO_2R) + NaOH.$$

The free acid HCO_2R combines with an undissociated molecule of the original salt $NaCO_2R$ to form an acid salt $NaH(CO_2R)_2$. *This acid salt is a colloidal substance*, and exists in colloidal suspension in the soap solution, in equilibrium with the ions and molecules of the original salt and of the NaOH.

The capacity for being coagulated and precipitated, which is characteristic of colloidal matter, is shown by the soap. Most *sodium salts will coagulate a soap solution* and precipitate the soap as a curd. The acid salt $NaH(CO_2R)_2$ seems to collect (**absorb**) and carry down with it the most of the sodium hydroxide. As both of the substances on the right of the equation (above) are thus precipitated, the equilibrium is displaced to the right, and the precipitation becomes complete. This explains * the process of "salting out" which plays so large a part in the manufacture of soap.

504. Causes of the Cleansing Action of Soap. The chief use of soap solution is in removing grease and dirt from yarn, cloth, or clothing, and from woodwork and kitchen utensils. Soap solution has *two* more or less distinct properties, *one* of which enables it to remove oil or grease (viscous, insoluble liquids), and the *other* of which enables it to remove dust and dirt (largely minute, solid particles of carbon — soot). The

---

* "Salting out" is often explained as being due to the increased concentration of sodium-ion causing the normal ion-product of the soap to be exceeded. This theory falls to the ground when we consider the facts, namely, that precipitation by excess of one ion is (1) confined to saturated (or nearly saturated) solutions, and (2) leaves the solution saturated still, while salting out works with dilute solutions of soap and even then gives almost *complete* precipitation.

former is its *emulsifying power*, the latter is probably connected with its nature as a *colloidal suspension.*

505. The Emulsifying Action of Soap. — How Soap Removes Grease. When an insoluble oil, such as kerosene or lubricating oil, is shaken with water it is divided into minute droplets separated by water from one another. When the shaking ceases, however, the droplets begin to run together and soon the oil and water have separated once more into two layers of transparent liquid. When very dilute soap solution and oil are shaken together, however, the droplets do not run together, but remain permanently suspended. The mixture is opaque and more or less viscous. Such a **permanent mixture of two insoluble liquids** is called an **emulsion.**

Soap solution, when *rubbed* on oily or greasy goods, *emulsifies the grease,* converts it into droplets, surrounded by soap solution and separated from the cloth, and so permits it to be washed off.

In mayonnaise dressing, which is a thick, almost solid, permanent emulsion, the olive oil is emulsified by the colloidal matter of the yolks of the eggs which have been dissolved in the vinegar.

506. Adsorption of Colloidal Matter. When a solution containing colloidal substances, such as many dyestuffs and organic coloring matters, is shaken with finely pulverized charcoal or with infusorial earth, the colloidal substance adheres to the surface of the powder (is **adsorbed**) and the liquid is consequently decolorized. This principle is used in decolorizing the extracts in sugar-refining (p. 182), and in "bleaching" oils.*

When dilute soap solution is shaken with infusorial earth and the mixture is filtered, the clear liquid is found to have

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* Non-colloidal substances, such as gases (hydrogen sulphide and ammonia), are also adsorbed by charcoal.

been deprived of the soap. The soap is evidently precipitated (adsorbed) on the surface of the particles of the solid.

507. How Soap Removes Dirt. Clearly there is a tendency to cohesion between the colloid in a soap solution and the particles of a fine powder. When there is much of the powder, and little of the soap in solution, the powder takes the soap out of the solution. When, however, there is much of the colloid in the form of soap solution, and little of the solid, and that very finely divided, the same tendency to adsorption exists, *only, in this case, the colloidal particles carry off the powder*. In short, the dirt is removed by adsorbtion into the solution.

508. Possible Objections to the Foregoing Explanation. Formerly, soap solution was supposed to remove grease (and soot?) because of its slight alkaline reaction, due to hydrolysis. This explanation must be given up, because: (1) an alkali so dilute that it exists in equilibrium with the free fatty acid, can not possibly saponify the *ester* contained in a grease spot. (2) Pure alkali of the same concentration (or stronger) has no more emulsifying power than water. Such an alkaline solution will indeed emulsify an animal or vegetable oil (cod-liver oil, cotton oil, castor oil), but it does so by interacting with the free fatty acid always present in such oil (p. 300) and *forming therefrom a soap.* Such an alkaline solution does *not* emulsify kerosene, although soap solution does. The emulsifying agency is always a soap. (3) Very dilute alkali has no more effect upon soot than has water, — but soap solution takes clean (greaseless) soot instantly into permanent suspension.

The power of forming an emulsion depends, theoretically, upon the *abnormally low surface tension* of dilute soap solution. Very dilute alkali has the same high surface tension as has pure water.

509. Exercises.

1. Which reactions of acids are shown by palmitic, stearic, and oleic acids, and which are not shown?

2. Make equations for the formation of: (a) ethyl formate; (b) glyceryl formate; (c) ethyl stearate.

3. Make equations for the action of superheated water on: (a) stearin, and (b) olein; and for the action of caustic soda on: (c) stearin, and (d) ethyl acetate.

4. Summarize the facts which show soaps to be salts.

5. (a) Make the equation for the hydrolysis of sodium palmitate. (b) What reaction (acid or alkaline) should soap solution possess, and why (p. 282)?

6. Why does "French dressing" (vinegar, salt, and olive oil) give an emulsion, which is much less durable than mayonnaise dressing?

CHAPTER XXXII.

EXPLOSIVES AND PLASTICS.

510. Although very different, in their ordinary uses, from the fats, modern explosives are nevertheless esters, and closely connected in chemical nature with these inert substances. Stranger still, the material of the celluloid hair comb is chemically an ester of the explosive type. And strangest of all, imitation silk, as lustrous as the product of the silk-worm, is made by hydrolyzing esters like guncotton.

511. Nitroglycerine. As already mentioned, the alcohols interact with inorganic acids, as well as with organic ones, to produce esters. A familiar illustration is met with in the manufacture of nitroglycerine (glyceryl trinitrate) by the action of glycerine and nitric acid:

$$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(NO_3)_3 + 3H_2O.$$

To assist in the liberation of the water, the nitric acid is mixed with a dehydrating agent. The glycerine is then added slowly to the cooled reagents. The nitroglycerine is an almost *colorless oil* which floats to the surface of the acid mixture. It is shaken repeatedly with water, in which it is insoluble, and then with sodium carbonate solution, in order to free it from all traces of the acids.

Nitroglycerine *explodes* violently, often from the slightest shock. It owes this power to the fact that its carbon and hydrogen can combine with the oxygen it contains to form carbon dioxide and water:

$$2C_3H_5(NO_3)_3 \rightarrow 6CO_2 + 5H_2O + 3N_2(+ O).$$

The latter are very stable substances and much heat is liberated in forming them. They are both produced as gases and, at the high temperature of the action, they and the nitrogen tend to occupy a great volume — or to exert an enormous pressure in the effort to do so.

The explosion is also so *sudden*, compared with that of gunpowder, that nitroglycerine would shatter the breech of a rifle before the bullet had time to move. It also pulverizes rock, instead of breaking it into fragments of usable size. For these reasons, as well as on account of the danger in handling, and impossibility of safely transporting the substance, it is made into blasting gelatine (see below). The old form of dynamite was made by soaking a porous earth (infusorial earth, kieselguhr) with nitroglycerine.

512. Guncotton or Cellulose Nitrate. Cotton is composed of cellulose $(C_6H_{10}O_5)_y$, a substance which has chemically much in common with glycerine and the alcohols. When cotton is steeped for half an hour in a cooled mixture of nitric and sulphuric acids, it is converted into cellulose trinitrate or guncotton:

$$C_6H_7O_2(OH)_3 + 3HNO_3 \rightarrow C_6H_7O_2(NO_3)_3 + 3H_2O.$$

The fibers have the same appearance as before, but are crisper to the touch. The guncotton is washed thoroughly with water to remove the acids, which would cause slow decomposition and perhaps accidental explosion.

Dried guncotton burns briskly (deflagrates) when set on fire. While wet, it can be moulded and cut without danger. It explodes only when "set off" by a small amount of another explosive. Fulminate of mercury $Hg(ONC)_2$, used in percussion caps, is commonly employed. By such means the explosion is brought about in wet guncotton as easily as in dry.

In pure form guncotton is used only in torpedoes and submarine mines. Like nitroglycerine it explodes too rapidly to be used in fire-arms or for blasting.

The fact that a flat rock or plate of steel is shattered, when a charge explodes upon its surface, does not show that the substance "explodes downwards only." The explosion strikes the air with as much violence as it strikes the rock. The *effect* on the air escapes notice, because it is not permanent. That on the rock or steel plate remains, however, because the solid is shattered.

513. Smokeless Powder and Dynamite. The violence of guncotton is reduced by compressing it, and still more by dissolving it and allowing the solvent to evaporate. Thus, **cordite** is made by dissolving guncotton (65 parts), nitroglycerine (30 parts) and vaseline (5 parts) in acetone. The resulting paste is rolled and cut into pieces of different dimensions, according to the rate of explosion desired. When the acetone evaporates, the horny cordite remains. These explosives are *smokeless* because they differ from gunpowder (p. 287) in yielding no solids when they decompose.

Blasting gelatine, giant powder, and other forms of **dynamite** are made by dissolving guncotton in nitroglycerine. Substances like nitrate of sodium or of ammonium and sawdust or flour are added to adjust the rate of explosion so that, for example, coal may be split up, but not shattered.

514. Celluloid, Collodion, Artificial Silk. A special guncotton, less completely "nitrated" by the nitric acid, when worked between rollers with camphor and a little alcohol, forms a viscous solution. When the alcohol evaporates, a transparent colorless solid, **celluloid,** remains. Photographic films are made by rolling the dough into sheets. Fillers and dyes can be added to the dough and the latter can be moulded to any form. In this way ivory-like or black combs and brush handles, opaque white knife handles, articles of "artificial amber" and so forth can be made.

The same sort of guncotton dissolves in a mixture of alcohol and ether, giving a solution called **collodion,** used in photography and in medicine.

When collodion is forced under great pressure through minute holes in a steel die, the threads dry as they issue from the openings and can be wound on spools. The product is treated with an alkali, which saponifies the ester (p. 302). This "denitration" destroys the explosive qualities, leaving a material of the composition of the original cotton. The product is one of the forms of **artificial silk,** and is at least as brilliant in appearance as the real article.* It can be dyed to any desired tint.

515. Cellulose Acetate. When cotton is treated with acetic acid (in the form of acetic anhydride) it gives another ester, **cellulose acetate.** The viscous liquid dries to a tenacious film. On account of its waterproof character and non-conductance of electricity, it is now used for insulating electric wires. Artificial horsehair (*e.g.* for making women's hats) and bristles for hair brushes are made of it.

516. Other Plastics from Cellulose. Although the chemical reactions involved probably do not fall within the class considered in this chapter, some other applications of cellulose may conveniently be mentioned here.

Cellulose dissolves in hot, concentrated zinc chloride solution. When the liquid is pressed through a small orifice into alcohol, the cellulose is precipitated in the form of a thread. By carbonizing, this is made into **filaments** for incandescent electric lamps.

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* Real silk is a protein (§§ 569, 585), and is not chemically related to cellulose.

Cellulose, such as paper (wood pulp), is soluble also in a solution of cupric hydroxide in excess of ammonium hydroxide, and is reprecipitated by dilute sulphuric acid. Paper or cotton goods can be passed through, first one and then the other of these liquids, and so receive a tough, **waterproof** surface. **Artificial silk** is made by pressing the solution through dies into the precipitant.

Cotton, when dipped in strong sodium hydroxide solution, and then stretched while being washed with hot water, acquires a brilliant luster and is used in enormous quantities under the name of **mercerized cotton** (discovered by John Mercer).

Finally, mercerized cotton, or wood pulp treated with caustic soda, combines with carbon disulphide to give **viscose.** Viscose dissolves in water, and decomposes in solution giving a plastic form of cellulose. This can be rolled into transparent sheets, made into caps for bottles, moulded into any form, or pressed through dies into solutions of salts of ammonium to give still another form of artificial silk.

517. Bakelite, Another Plastic. Not chemically related to the preceding plastics is **bakelite,** prepared from formaldehyde CH_2O and phenol C_6H_5OH (carbolic acid). Under suitable heat treatment the mixture gradually sets to a solid, hard, infusible, resinous mass, which is insoluble in all known solvents. Before it sets, it can be dyed or "filled," and it can be applied as lacquer, or moulded to any form. Switch boards, dolls, ornamental buttons, artificial jewels, phonograph records, billiard balls, and stereotyping matrices are amongst the objects into which it is now fashioned.

518. Exercises.

1. What chemical change would occur after mixing nitroglycerine with sodium hydroxide solution? Name the kind of reaction and give the equation.

2. When nitroglycerine explodes, in what relative volumes are steam, carbon dioxide, and nitrogen produced? What principle is used in answering this question?

3. Make an equation for the decomposition of guncotton, similar to that given for nitroglycerine (p. 310).

4. Make an equation for the denitration of guncotton by an alkali.

5. In view of the statement on p. 187, make a list of the substances which do react with cellulose.

CHAPTER XXXIII.

CALCIUM AND ITS COMPOUNDS.

519. Up to this point our attention has been given largely to non-metallic elements and to negative radicals (*e.g.* NO_3) and the compounds related to them (*e.g.* NO, N_2O, NO_2). Having now disposed of most of these elements and radicals, we enter upon the systematic study of the *metallic* elements, and the radicals (mainly positive) and compounds which contain them. We have been prepared for this by a detailed discussion of two typical metallic elements, namely sodium and potassium, and by a more casual examination of some of the compounds of arsenic, antimony, and bismuth.

520. The Calcium Family. Calcium belongs to a family of metallic elements which includes also strontium, barium, and radium. This family resembles that to which sodium and potassium belong in so far that the metals are second in activity only to the two last named and that the hydroxides are active bases. The chief *differences* are that the metals of the present group are *bivalent* and that all the carbonates and many other single compounds are *insoluble.*

Compounds of calcium confer a *brick-red color* upon the Bunsen flame.

521. Calcium. The metal is made by electrolyzing melted calcium chloride in a graphite crucible, which forms the anode. The cathode, to which the negative wire is attached, is a rod of iron, one end of which dips into the fused salt. The calcium, liberated at this point, adheres to the rod. The latter is slowly raised, in such a way that the calcium always remains in contact with the liquid. In this fashion a long "cabbage-stalk" of calcium is finally produced.

The metal is slightly harder than lead and has a *silver-white* luster. It is the fifth metal in the order of electrical *conductivity*. It *decomposes cold water*, liberating hydrogen (pp. 39, 42). It is easier and safer to use for this experiment than sodium, because it sinks to the bottom, does not melt, and reacts rapidly but not violently. It tarnishes rather gradually, but *burns* brilliantly when heated with a blast lamp to a temperature above its melting-point.

522. Calcium Carbonate $CaCO_3$. The carbonate is the commonest compound of calcium. White **marble** is a pure variety, composed of crystals compactly wedged together. **Limestone** does not show much crystalline structure and usually contains clay and other impurities. **Chalk** is made up of shells of minute marine organisms. **Shells, coral, and pearls** are likewise mainly calcium carbonate. Well-formed crystals (calcite, Iceland spar — Fig. 78 — and dog-tooth spar — Fig. 79) are common.

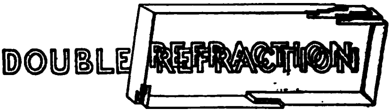

Fig. 78

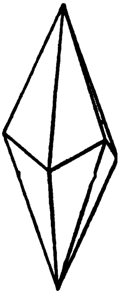

Fig. 79

Limestone is *used* for building and in road-making. Much of it is employed in making quicklime, cement, and glass (§ 451), and as a flux in metallurgical operations (see § 596). Marble, often variegated by the presence of impurities, is used in building and sculpture.

As we have seen (p. 158), calcium carbonate ***reacts with acids*** to give carbonic acid:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2CO_3 \rightarrow H_2O + CO_2 \uparrow$$

When heated, all forms of calcium carbonate give off carbon dioxide, and leave calcium oxide (see below):

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

523. Calcium Oxide CaO, Manufacture. The manufacture of calcium oxide or **quicklime** (*i.e.* live lime) is one of the most ancient chemical industries. The limestone is thrown into a kiln lined with brickwork (Fig. 80). The flames and heated gases from the fire pass through the limestone and the carbon dioxide is liberated and carried off by the draft. When this *gas* is to be used, as in the Solvay process or in the refining of sugar, coke (smokeless) is chosen as the fuel. When no use is to be made of the escaping gas, coal may be employed.

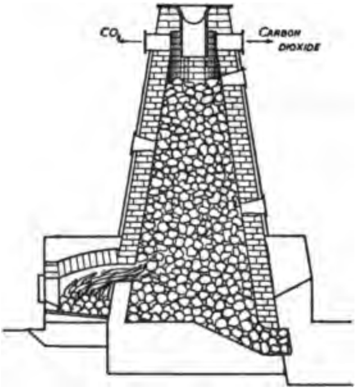

Fig. 80

The use of as low a temperature as possible is important. A high temperature causes the impurities in the limestone (the clay, etc.) to interact with the quicklime and form fusible silicates, which fill the pores and retard the subsequent action of water in slaking the lime. Calcium carbonate gives a pressure of only 25 mm. of carbon dioxide at 700° and one atmosphere at about 900°. The action is reversible (see equation), and if the gas lingers in the kiln, the carbon dioxide recombines with the quicklime as fast as it is liberated

— unless a temperature above 900° is used. When, however, the gas is continually removed, the backward action is prevented, and a lower temperature suffices to complete the dissociation of the compound. Hence a low temperature and a good draft of air through the kiln are essential.

524. Properties and Uses of Quicklime. Calcium oxide is a *white, amorphous* material. It melts only in the electric arc. When heated strongly, it *glows* with an unusually brilliant and white light. The **Drummond,** or **oxy-hydrogen** light, more commonly called the **lime light** or **calcium light,** is produced by allowing a flame of burning oxygen and hydrogen or illuminating gas to play upon a cylinder of calcium oxide (Fig. 81). The gases are contained in iron cylinders, under pressure, and so the apparatus can be used for illumination or projection where neither electricity nor a local supply of gas is available.

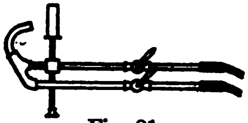

Fig. 81

When *water* is poured upon quicklime, it is at first absorbed, and then enters into combination to form calcium hydroxide (slaked lime, see § 525):

$$CaO + H_2O \rightarrow Ca(OH)_2.$$

So much heat is given out that the excess of water is converted into steam. The quicklime swells and falls to powder.

Quicklime is used most largely in making slaked lime for mortar, and also in the manufacture of bleaching powder. Other uses are mentioned under the hydroxide.

Quicklime deteriorates when exposed to the air. It combines both with the moisture and carbon dioxide in the atmosphere and becomes *air-slaked.*

525. Calcium Hydroxide $Ca(OH)_2$. The hydroxide is a *white, amorphous* powder. It is slightly *soluble* in water (about 1 : 600 at 18°), giving **lime-water.** The solution has a strong *alkaline reaction,* however, showing that so much as is dissolved is very largely ionized. **Milk of lime,** a saturated solution with a large excess of calcium hydroxide suspended in it, is employed in many operations (see *e.g.* §§ 533, 562). As the dissolved part undergoes chemical change, more goes into solution. Being cheap, it is used whenever an alkali is needed, provided a dilute alkali will serve the purpose. It interacts with acids giving salts of calcium, and shows the other properties of a base (p. 138).

Slaked lime is used in making mortar (see § 526) and alkalies (p. 121) and in purifying sugar (p. 182). It is employed to remove the hair from hides, before tanning, an action which recalls the solubility of wool (sheep's hair) in an alkali * (p. 1). It finds application, also, in softening water (§ 533) and as whitewash.

526. Mortar. Mortar is made by mixing slaked lime with three or four times its bulk of sand, and making the whole into a paste with water. When the water evaporates, a porous, rather crumbly material remains. This, however, at once begins to harden, owing to the action of the carbon dioxide in the air upon the lime:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \uparrow$$

The crystalline calcite ($CaCO_3$) adheres to, and is interlaced with the sand, and gives a rigid, though porous, structure attached firmly to the brick or stone. The pores facilitate the penetration of the air into the deeper parts and thus provide, both for the fresh supplies of carbon dioxide required for the continuance of the action shown in the equation, and

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* Depilatory preparations consist usually of calcium sulphide CaS, and are applied as a paste with water. The sulphide is hydrolyzed, and the calcium hydroxide dissolves the hair without injuring the skin.

for a considerable amount of useful ventilation through walls of the building.

527. Basic Oxides. An oxide which combines (directly or indirectly) with water, giving a base, is called a basic oxide (p. 217). Such an oxide (*e.g.* CaO) is always an oxide of a metallic element. All oxides of metallic elements are not basic, however (*e.g.* Mn_2O_7 and CrO_3, Chap. XLI, are acid anhydrides).

The basic oxide is often used *instead* of the base, and gives the *same* compounds. For example, acids act upon calcium oxide, giving salts, just as they do with calcium hydroxide (p. 128):

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O.$$

$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O.$$

Acid anhydrides also combine directly with basic oxides to give the same salts which they form when acting upon the hydroxide.

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \text{(p. 318).}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad \text{(p. 320).}$$

528. Calcium Sulphate $CaSO_4$, Various Forms. Calcium sulphate is a very common mineral. It occurs, as **anhydrite** $CaSO_4$, in the salt deposits. **Gypsum** $CaSO_4,2H_2O$ is found in masses, and also in single crystals (selenite, Fig. 33, p. 88). **Alabaster** is highly crystalline gypsum, tinted by impurities.

529. Properties and Uses. **Gypsum** $CaSO_4,2H_2O$ is the commonest form, and is the one produced when calcium sulphate is precipitated. It is white and much softer than calcite. It is only slightly soluble in water (1 : 500 at 18°). It is used in making plaster of Paris and is the chief component of blackboard "crayon."

When gypsum is heated, the vapor pressure of the water it gives off (p. 55) soon exceeds that of the moisture in the atmosphere, and the compound begins to decompose:

$$2CaSO_4,2H_2O \rightleftarrows (CaSO_4)_2,H_2O + 3H_2O \uparrow$$

The hemi-hydrate which remains (**plaster of Paris**) gives a much lower pressure of water vapor and is more stable.

530. Plaster of Paris $(CaSO_4)_2,H_2O$. The hemi-hydrate is manufactured in large quantities by heating gypsum in kilns. When moistened with water, it sets in about half an hour to a solid mass of gypsum. The temperature used in making it must not exceed 125°, otherwise the hemi-hydrate is itself decomposed, the plaster is "dead burnt," and it no longer sets readily. The setting involves, simply, the reversal of the equation given above.

Plaster of Paris swells somewhat, in setting, and so fills out completely every detail of a mould and applies itself closely to the outline of an object on which it is spread. It is used in making casts, and in surgical bandages where movable parts are to be held rigidly in place. **Stucco** is made with sizing or glue instead of pure water.

Casts are made smooth and non-porous ("ivory" surface) by a coating of paraffin which fills the pores. Excellent imitations of bronze or other castings are produced by rubbing with pulverized metals.

531. Hard Water, Its Contents. All natural waters except rain water, which is "soft," contain salts of calcium and magnesium in solution and are more or less "hard." These salts are dissolved by the water in its passage over and through the soil.

Although limestone is very insoluble in pure water (0.013 g. per liter), yet it interacts with the carbonic acid contained in all natural waters, giving **calcium bicarbonate** which is about thirty times more soluble:

$$CO_2 + H_2O \rightleftarrows H_2CO_3 + CaCO_3 \rightleftarrows Ca(HCO_3)_2.$$

When the water is boiled, these actions are all reversed. The carbon dioxide is driven out of solution, the carbonic acid is decomposed, and the calcium bicarbonate gives calcium carbonate, most of which is at once precipitated. Iron carbonate is also held in solution as bicarbonate $Fe(HCO_3)_2$ and is precipitated as $FeCO_3$ by boiling. These two bicarbonates constitute **temporary hardness.** Their decomposition causes the " fur " in a kettle.

The sulphates of calcium (solubility 2 g. per liter) and of magnesium (very soluble) are also commonly found in natural waters. These salts are not altered by boiling and, along with magnesium carbonate (sol'ty 1 g. per l.) and calcium carbonate (sol'ty 0.013 g. per l.), give **permanent hardness** to the water.

Hardness is estimated in "degrees." In France, and commonly in the laboratory, 1 part of $CaCO_3$ (or its equivalent of other salts) per 100,000 (0.01 g. per liter) constitutes one degree. In the United States one degree is 1 grain per gallon of 58,333 grains (0.017 g. per l.). In Britain one degree is 1 grain per gallon of 70,000 grains (0.014 g. per l.). Well water, originating in chalk or limestone formations, may have 37° (Fr.) or more of hardness.

532. Consequences of Hardness in Water. When hard water is used in a steam boiler, the salts, of course, are not carried off with the steam, but accumulate amazingly as fresh water is injected and steam alone is drawn off. In time, heavy deposits of *boiler crust* settle on the tubes of the boiler, and interfere with the transference of heat from the metal to the water. One-fourth of an inch of crust will increase the bill for fuel by 50 per cent. In addition to this the iron is heated to a higher temperature and may even become red hot. In consequence, it combines more rapidly with oxygen on the outside and displaces hydrogen from the water (p. 39) on the inside, giving in both cases Fe_3O_4. Thus the life of the boiler is shortened. If the formation of the crust is not prevented (§ 533), or if the crust is not removed, the boiler may explode and great damage may be done.

When hard water is used for *washing*, in the *household* or *laundry*, much soap has to be dissolved before the necessary lather can be secured. The soap (sodium palmitate, etc., p. 302) interacts by double decomposition with the salts of calcium and magnesium, giving palmitates, stearates, and oleates of these metals. These salts are insoluble and form a "curd." With sodium palmitate, for example, the action is

$$CaSO_4 + 2Na(CO_2C_{15}H_{31}) \rightarrow Ca(CO_2C_{15}H_{31})_2 \downarrow + Na_2SO_4.$$

Not until all the salts causing the hardness have been decomposed, does the permanent solution of soap which is required for washing begin to be formed. This waste is often very great and expensive. Thus, calculating from the equation, with 1° (U.S.) of hardness, 100 gallons (U.S.) of water should use up 0.075 pound of soap (1° Brit. and 100 gal. Brit., 0.075 lb.). In point of fact, however, twice these equivalent amounts of soap are wasted, because the colloidal calcium salts carry down with them more than an equal amount of undecomposed soap. Hence measurement shows that, with 1° (U.S. or Brit.) of hardness, 100 gallons (U.S. or Brit.) of water actually destroy 0.17 pound of soap. Thus, with 35° no less than 6 pounds of soap are wasted per 100 gallons, before the part of the soap that is to do the work begins to dissolve.

533. Treatment of Hard Water. The temporary hardness can be removed by boiling the water, or using some preheating arrangement in connection with the boiler (stationary engines only).

Temporary hardness is commonly removed, on a large scale, by adding *slaked lime* (made into milk of lime) in *exactly the quantity* shown by an analysis of the water to be required, and stirring for a considerable time:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O. \qquad (1)$$

The bicarbonate is neutralized and all the lime precipitated. The latter is removed by filtration.

Permanent hardness is not affected by slaked lime, but is precipitated by adding sodium carbonate in the necessary proportion:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4. \qquad (2)$$

When *both kinds of hardness* are present, crude caustic soda (sodium hydroxide) may be employed. It neutralizes the bicarbonate, precipitating $CaCO_3$:

$$Ca(HCO_3)_2 + 2NaOH \rightarrow CaCO_3 \downarrow + Na_2CO_3 + 2H_2O \qquad (3)$$

and giving sodium carbonate. The latter then acts as in equation (2).

Instead of this, the treatments indicated in equations (1) and (2) may be applied in combination (Porter-Clark process).*

In the new **permutite process** the water is simply filtered through an artificial sodium silico-aluminate (permutite $Na\overline{P}$) which is supplied in the form of a coarse sand. The calcium, etc., in the water is exchanged for sodium, which does no harm:

$$Ca(HCO_3)_2 + 2Na\overline{P} \rightarrow 2NaHCO_3 + Ca\overline{P}_2.$$

After twelve hours' use, the permutite is covered with 10 per cent salt solution and allowed to remain for the other twelve hours of the day, when it is ready for employment once more:

$$2NaCl + Ca\overline{P}_2 \rightarrow CaCl_2 + 2Na\overline{P}.$$

---

* So far as the hardness is due to magnesium bicarbonate, a *double* proportion of lime must be added to precipitate the magnesium as hydroxide (sol'ty 0.01 g. per 1.), because the carbonate is too soluble (1 g. per 1.).

Only salt, which is inexpensive, is consumed, and calcium chloride solution is thrown away. Permutite removes magnesium, iron, manganese, and other elements in the same way. The life of a charge is said to be over twenty years.

534. Hard Water in the Laundry. As we have seen (p. 324), soap will soften water, but the calcium and magnesium salts of the soap acids, which are precipitated, are sticky, and soil the goods being washed. Other substances that soften water not only give non-adhesive precipitates, but are also much cheaper, and an attempt is generally made to utilize them. The use of slaked lime is impracticable on a small scale.

Washing soda $Na_2CO_3,10H_2O$ is added to precipitate both kinds of hardness:

$$Ca(HCO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaHCO_3$$
$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4.$$

The small amounts of salts of sodium which remain in the water have no action on soap.

Household Ammonia NH_4OH acts like sodium hydroxide (§ 533):

$$Ca(HCO_3)_2 + 2NH_4OH \rightarrow CaCO_3 \downarrow + (NH_4)_2CO_3 + 2H_2O$$
$$CaSO_4 + (NH_4)_2CO_3 \rightarrow CaCO_3 \downarrow + (NH_4)_2SO_4$$

except that it will *not* precipitate magnesium-ion.

Borax $Na_2B_4O_7,10H_2O$ (p. 275) is hydrolyzed and the sodium hydroxide contained in its solution acts as already (§ 533) described.

The supposed bleaching or whitening action of borax or soda is a myth; these salts *prevent staining by the iron* in the water. They simply precipitate the iron (present as $Fe(HCO_3)_2$), which almost all waters contain, as $FeCO_3$, *before* the goods are put in. This precipitate is easily washed out in rinsing. The palmitate, etc., of iron, however, which the soap itself would throw down, is sticky and adheres to the cloth. The air subsequently oxidizes it (see § 612) and gives hydrated ferric oxide (rust), which is brownish-red.

It is evident that, properly to achieve their purpose, the soda and borax must be added, must be completely dissolved, and must be allowed to produce the precipitation of $FeCO_3$, $CaCO_3$, etc., all *before* the soap (or the goods) is introduced. If the soap is dissolved before or with the soda, *it* will take part in the precipitation, and give sticky particles containing the iron and calcium salts of the soap acids.

The soda, borax, and ammonia do not themselves remove dirt — that is done by the dissolved soap (p. 306). With the help of rubbing, however, they do emulsify and remove animal or vegetable oil and grease, but not mineral oil (§ 508), when these happen to be on the goods. But soap alone will do this also, and remove mineral oil as well.

Washing powders are, or ought to be, mainly sodium carbonate, mixed with more or less pulverized soap.

535. Calcium Chloride, $CaCl_2$. Chloride of calcium is obtained as a by-product in the Solvay process (p. 278) and in other industries. It crystallizes from water as the white, hexahydrate, $CaCl_2,6H_2O$, and is very soluble. It has few applications. The porous, granular variety, used for drying gases, is made by driving most of the water out of the hexahydrate by heat. The granular form is used in large amounts for sprinkling on dusty roads. The salt, being deliquescent (p. 90), attracts water from the air and moistens the dust with calcium chloride solution. The saturated solution does not freeze until −48° is reached, so that chilled calcium chloride brine is used in refrigerating appliances (p. 206).

536. Calcium Cyanamide $CaCN_2$. Calcium carbide, when strongly heated, absorbs nitrogen, giving a mixture of calcium cyanamide and carbon (**nitro-lime**):

$$CaC_2 + N_2 \rightarrow CaCN_2 + C.$$

When treated with hot water, the product is decomposed into calcium carbonate and ammonia:

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3.$$

Calcium cyanamide is now manufactured for use as a *fertilizer*. In the moist, cold soil the action is probably not so simple as that shown in the above equation, but it finally provides combined nitrogen in a form that can be absorbed by plants.

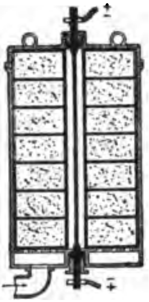


Fig. 82

At Odda (Norway) the carbide is pulverized and placed in a cylindrical furnace (Fig. 82), holding 300 to 450 kg. The heat (800 to 1000°) is furnished by the passage of a current of electricity through a thin carbon rod, which passes through the axis. The tube surrounding the rod and the other partitions are of cardboard, which burns up and leaves openings for the circulation of the nitrogen. The latter is made by the fractionation of liquid air and is introduced under pressure. In thirty-five hours nitrogen ceases to be absorbed, and the product is pulverized when cold.

Nitro-lime, when fused with sodium carbonate, gives **sodium cyanide** NaNC, used in the extraction of gold:

$$CaCN_2 + C + Na_2CO_3 \rightarrow CaCO_3 + 2NaNC.$$

537. Other Compounds of Calcium. Calcium **fluoride** CaF_2 occurs as a mineral (**fluorite**). It is our source of hydrofluoric acid (p. 258), and is used in metallurgy to lower the melting-point of slags. The **phosphates** (p. 264) and **bisulphite** (p. 221) of calcium, and **bleaching powder** CaCl(OCl) (p. 234) have already been discussed.

538. Exercises.

1. Why can not lime-water be kept in an open bottle?
2. Why does whitewash become so firmly attached to the wall?
3. When the water drips from the tap into a porcelain basin, a brown

stain is gradually produced. Explain (see § 612). Make equations for the action, assuming the product to be Fe_2O_3.

4. Make equations for the action of sodium palmitate: (a) upon calcium bicarbonate; (b) upon magnesium sulphate.

5. In softening water: (a) what would be the objection to using an excess of milk of lime; (b) why is prolonged stirring required (§ 525); (c) why must the precipitate be removed by filtration?

6. (a) Why do small amounts of sodium salts have no action on soap? (b) What effect would large amounts have?

7. Explain why wood ashes are sometimes used to soften water, and how they act.

8. Make an equation for the action of chlorine-water upon calcium hydroxide.

9. Why does fluorite lower the melting-point of a slag?

CHAPTER XXXIV.

MAGNESIUM AND ZINC.

539. We can most easily remember magnesium and zinc by the facts that they are silver-white metals with a markedly crystalline structure, and that they displace hydrogen from dilute acids. In these respects they resemble aluminium, but the latter is trivalent in all its compounds, while the present two elements are bivalent exclusively (see Periodic System).

MAGNESIUM Mg.

540. Occurrence. Magnesium carbonate is found in **dolomite** $CaCO_3,MgCO_3$, a common rock, and in small amounts as **magnesite** $MgCO_3$. The sulphate and chloride are found at Stassfurt. Several natural silicates of magnesium, such as **meerschaum, asbestos, talc** or **soapstone,** and **olivine,** are familiar minerals.

Asbestos, a fibrous material, is used in making fireproof cloth and cardboard. Soapstone is made into sinks and table tops for use, for example, in laboratories. These materials can be made coherent with sodium silicate (p. 272).

541. The Metal Magnesium. The metal is made by electrolyzing a molten mixture of magnesium, potassium, and sodium chlorides. A carbon rod forms the anode, and the iron crucible the cathode, on which the metal collects in globules. The mass, when cold, is broken up and the metal is recast in bars. The metal can be drawn, through a die, into ribbon or wire.

Magnesium *rusts* in the air, gradually crumbling to a white powder of a basic magnesium carbonate. It *displaces hydro-*

gen slowly from boiling water, and very rapidly from cold dilute acids. It *burns* in air, with a brilliant white light, producing a mixture of the oxide MgO and nitride Mg_3N_2 (see argon, p. 198). Magnesium filings, mixed with 1.7 parts of potassium chlorate, give **flash-light powder.** Signal (Bengal-) lights are made of shellac, barium nitrate, and magnesium powder. The whole annual production of the metal is probably not over 20 tons.

542. Oxide MgO and Hydroxide $Mg(OH)_2$. The **oxide** is made by heating magnesium carbonate, and is therefore called **calcined magnesia.** Being very infusible ("refractory") it is used in lining electric furnaces. It combines slowly with water, giving the **hydroxide** $Mg(OH)_2$, which with water gives a mortar that hardens under the action of the carbon dioxide of the air (see mortar, p. 320). The oxide is *basic* (p. 321), and with acids gives salts by double decomposition.

Magnesium hydroxide $Mg(OH)_2$, being insoluble, is easily precipitated by adding sodium hydroxide to a solution of a salt of magnesium. When moistened and mixed with a little magnesium chloride, it sets to a hard basic chloride $(Mg(OH)_2)_x(MgCl_2)_y,(H_2O)_z$ of variable composition. The mixture, to which sawdust is sometimes added, is used as a plaster in house decoration.

543. Salts of Magnesium. Magnesium carbonate $MgCO_3$ is found in nature. That made by precipitation is a basic carbonate $3MgCO_3,Mg(OH)_2$, **magnesia alba,** which is used in tooth powder and for polishing silver.

Magnesium sulphate $MgSO_4$ is commonly sold as the heptahydrate, $MgSO_4,7H_2O$, **Epsom salt.** It is found in the salt deposits and in many aperient mineral waters. Thus **Hunyadi water** contains little beside 47 g. Epsom salt and 52 g. sodium sulphate ($Na_2SO_4,10H_2O$) and 1 g. sodium bicarbonate per liter. The salt is used for loading cotton goods and as a purgative.

Magnesium chloride $MgCl_2$ is found in sea water and in some natural waters. It is very deliquescent (p. 90) and, being present in impure table salt, causes the latter to cake, or even become moist in damp weather. Addition of a very little sodium bicarbonate to the salt remedies this difficulty. Magnesium chloride is a very objectionable form of hardness in water, because hot water partially hydrolyzes the salt and liberates hydrochloric acid, which attacks and corrodes the iron of the boiler and tubes. Hence sea water can not be used in marine boilers.

ZINC Zn.

544. Occurrence. Zinc is found as **zinc blende** ZnS (in large amounts in Missouri) and **smithsonite** $ZnCO_3$ (Spain and U.S.). While the metal was known before 500 B.C., it has only come into common use during the last century or so (first manufacture, Bristol, 1743).

545. Metallurgy of Zinc. In the case of the carbonate ore, the oxide ZnO is first obtained by heating. When zinc blende ZnS is the ore, it is crushed and pulverized, and then roasted to remove the sulphur and leave the oxide:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2.$$

The ore is fed in at the top of a huge, box-like furnace (Fig. 83, diagrammatic) through which rush the flames and heated gases from fuel gas burning with an excess of air. The ore is turned over, and gradually displaced forward by moving rakes until, at the end, it drops to the next level. Here it is raked in the opposite direction, until it falls to the third level. The ore collects at the bottom fully oxidized, while the sulphur

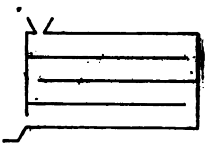


Fig. 83

dioxide in the gases is made into sulphuric acid. The oxide from either ore is then reduced by heating with powdered coal:

$$ZnO + C \rightarrow Zn + CO.$$

This treatment of zinc ores should be carefully considered. Since ores of most metals consist of the carbonate, sulphide, or oxide of the metal, these steps are common to most metallurgical processes. In the case of other metals, only the forms of the furnaces and other details vary.

In the case of zinc, because it is a *volatile* metal, the heating of the mixture of oxide and coal is conducted in *retorts*, from which the metal issues as *vapor*. The mixture is placed in fire-clay cylinders (4 to 5 ft. long), which are arranged in several tiers in an oblong, gas-heated furnace (Fig. 84). A fire-clay receiver is luted on with clay. The carbon monoxide burns with a blue flame at the nozzle of each receiver, while the zinc condenses to liquid within it. From time to time the liquid metal is raked out into a traveling iron pot, from which it is poured into moulds.

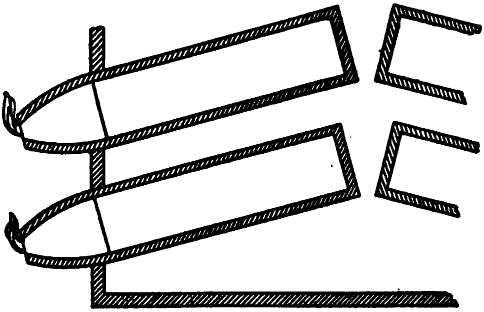


Fig. 84

546. Properties and Uses. The metal is *silvery* and crystalline. At 120 to 150° it can be rolled into sheets between hot rollers, at 200 to 300° it becomes brittle, at 419° it *melts*, and at 950° it *boils*. The *density* of the vapor shows it to be monatomic. Zinc vapor *burns* with a bluish flame, giving ZnO. In *air* the metal does not rust, being protected by a non-porous coating of a basic carbonate which adheres closely to the surface. Zinc displaces hydrogen from dilute *acids* (p. 40).

Sheet zinc is **used** for gutters and cornices, although for the latter purpose it is being displaced by terra cotta. Iron is coated (**galvanized**) with zinc by thorough cleaning with dilute sulphuric acid or the sand blast, and dipping in melted zinc. Iron netting, corrugated iron for sheds and roofing, and iron gutters, tanks, and pipes are coated, either in this way, or galvanically (see copper). **Sherardized** iron is made by covering the article with zinc dust and baking it. The zinc protects the iron, primarily because it excludes the air from the surface, and secondarily because, even when the coating is broken, the zinc, being the more active metal of the two (p. 42), is rusted first. Zinc is used also in extracting silver from crude lead (§ 663), as the active metal (anode) in batteries, and in several alloys (*e.g.* Babbitt's metal, p. 268, brass, and German silver). In the laboratory **granulated zinc,** made by pouring the melted metal in a thin stream into water, and **zinc dust** (impure, contains ZnO), are the forms commonly employed.

547. Zinc Oxide ZnO and Hydroxide $Zn(OH)_2$. The **oxide** is made by burning zinc vapor in air. It is *yellow* while *hot,* and *white* when *cold.* Mixed with oil, it is used as a *paint* (**Chinese white**). This has less covering power than has white lead paint (4 coats of the former equal 3 of the latter), but it does not darken from exposure to hydrogen sulphide in the air (ZnS is white, PbS black).

Zinc hydroxide $Zn(OH)_2$ is formed by precipitation. Both the oxide and hydroxide are *basic,* and give salts with acids.

But they are *also* somewhat *acidic*, and dissolve in excess of sodium hydroxide giving **sodium zincate** Na_2ZnO_2. When heated with a salt of cobalt, they give the *green* **cobalt zincate** $CoZnO_2$ (test).

548. Zinc Chloride $ZnCl_2$. The chloride is formed in the action of zinc or zinc oxide on hydrochloric acid. It is a *white, deliquescent* solid. Its aqueous solution *gelatinizes cellulose* and *dissolves it* (p. 313), and thus is used in parchmentizing paper and in impregnating wood to prevent decay. The aqueous solution is acid (hydrolysis) and is used for cleaning the surface of metals before *soldering* (p. 383). Solder "runs" on a hot brass, copper, or lead surface, *provided the latter is clean*, and adheres perfectly when cold. But it does not dissolve oxides, or melt them, and therefore can not even reach the surface of the metal, much less adhere to it, if the slightest tarnish is present.

549. Other Compounds. **Zinc sulphate,** $ZnSO_4$, $7H_2O$, is made by the action of sulphuric acid on zinc or zinc oxide. It is used in preserving hides and as a mordant in cotton printing (see dyeing, § 566). **Zinc sulphide** ZnS is precipitated (white) when **ammonium sulphide** $(NH_4)_2S$ solution is added to a salt of zinc:

$$ZnSO_4 + (NH_4)_2S \rightleftarrows ZnS \downarrow + (NH_4)_2SO_4 \text{ (dslvd.)}.$$

All double decompositions are reversible, but this one is practically complete. This is because ammonium sulphide, being a salt (p. 130), is highly ionized and gives much sulphide-ion $S^{=}$. When hydrogen sulphide is employed instead,

$$ZnSO_4 + H_2S \rightleftarrows ZnS + H_2SO_4,$$

only a part of the zinc is precipitated. The action comes to rest because the hydrogen-ion H^+ of the sulphuric acid competes with the zinc-ion Zn^{++} for the $S^{=}$, to form molecular

H_2S, and when a certain concentration of sulphuric acid (and therefore of H^+) has been reached, no more ZnS can be formed.

A mixture of zinc sulphide and barium sulphate $BaSO_4$, prepared in a special way, is called **lithopone.** Used as a white pigment, it has greater covering power than has white lead and is, besides, non-poisonous.

All the *soluble* compounds of zinc are somewhat poisonous.

550. Exercises.

1. (a) How do the electrolytic methods of making calcium and magnesium differ? (b) Why not electrolyze an aqueous solution of magnesium chloride in making magnesium? (c) Why use both potassium and sodium chlorides in making magnesium? (d) Why is magnesium, but not potassium or sodium, liberated?

2. Why are magnesium and zinc not found free in nature?

3. Why does magnesium rust completely (in time), while zinc does not?

4. Make equations for: (a) the action of magnesium on hydrochloric acid; (b) the burning of magnesium in air; (c) the heating of magnesium carbonate; (d) the precipitation of magnesium hydroxide from the sulphate; (e) the hydrolysis of magnesium chloride.

5. Why is salt containing magnesium chloride, after mixing with sodium bicarbonate, no longer deliquescent?

6. What is the density of zinc vapor (air = 1)?

7. Make equations for: (a) the action of hydrogen sulphide on zinc oxide; (b) the precipitation of zinc hydroxide; (c) the action of sodium hydroxide on zinc hydroxide.

CHAPTER XXXV.

ALUMINIUM.

551. The family of trivalent elements to which the metal aluminium belongs includes the non-metal boron (p. 274), and several rare metals.

552. Occurrence. Aluminium, although it does not occur free, is the third element in order of quantity. Its silicates, such as **clay** (kaolin) $HAlSiO_4$, **mica** $KAlSiO_4$, and **felspar** $KAlSi_3O_8$, are amongst the most plentiful minerals. The oxide Al_2O_3 occurs as **corundum, sapphire, ruby,** and **emery** (impure form). **Bauxite** is a valuable hydrated oxide. **Garnets** $Ca_3Al_2(SiO_4)_3$ are mined and pulverized to make " sand " paper. **Cryolite** $3NaF,AlF_3$ (Greek, *ice-stone*) is imported from Greenland.

553. Manufacture. The making of aluminium on a large scale originated in C. M. Hall's discovery (1886) that the oxide could be electrolyzed in solution in molten cryolite. Iron boxes (Fig. 85), about 5 by 3 feet and 6 inches deep, are lined with a compressed mixture of coke and tar which is afterwards baked. The lining forms the cathode, while the oxygen is liberated at the anodes — a series of rods of carbon about 3 inches in diameter which are attached to copper rods. The cryolite is melted (1000°) by the arcs struck by the car-

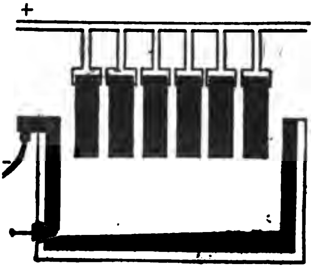


Fig. 85

bon rods. The latter are then raised somewhat, the aluminium oxide is added, and some coal (which floats) is thrown in to cover the surface and obscure the blinding glow. From time to time more of the oxide is added and the melted aluminium (m.-p. 650 to 700°) is tapped off. The oxide must be made from carefully purified bauxite, as the metal itself can not be purified commercially. In 1866 it cost $250 to $750 (£50–150) per kilogram and now sells at about 50 cents (2/–).

554. Physical Properties. The metal has a lower specific gravity (2.6) than any other metal that could be put to the same uses (sp. gr. iron 7.8, copper 8.8). It has malleability and the foil is taking the place of tinfoil to some extent for wrapping foods. It has considerable tensile strength, and is a good conductor of electricity. It is lacking in sufficient hardness and, when pure, can not be filed or turned because it adheres to the tools.

555. Chemical Properties. The metal *displaces hydrogen* rapidly from hydrochloric acid, it acts very slowly on dilute sulphuric acid, and hardly at all on cold nitric acid. In the *air* it acquires only a slight film of closely adhering oxide. This film prevents it from acting upon water (hot or cold). When the surface is cleaned and amalgamated with mercury, by dipping in mercuric chloride solution, however, this metal acts as a contact agent, and hydrogen is rapidly displaced:

$$2Al + 6H_2O \rightarrow 3H_2 \uparrow + 2Al(OH)_3 \downarrow$$

The foil, when heated, *burns* brilliantly in the air. When amalgamated (as above), it rusts in moist air with astonishing rapidity.

556. Uses. The largest quantity is consumed by steelmakers. When added in small amount (less than 1 : 1000) to molten steel, it combines with the gases, and gives sound ingots free from blow holes. Next to this comes its use for long distance transmission of electricity. A cable of the requisite capacity is larger than one of copper for the same current, but is lighter and puts less strain on the supports. Cooking vessels of aluminium are not corroded and are largely used. Cameras and opera glasses are made of it. Pulverized aluminium, mixed with oil, gives a paint which protects iron admirably.

Aluminium **bronze** (copper, with 5 to 12 per cent aluminium) has a brilliant golden yellow color and is stable in air and easily worked. **Magnalium** (containing 1 to 2 per cent of magnesium) can be filed, turned, or polished like a mirror, and is better for many purposes than the pure metal.

On account of its great chemical activity (p. 42), aluminium displaces many other metals (*e.g.* iron, manganese, and chromium) from combination (Goldschmidt, 1898). Thus powdered aluminium and oxide of iron when mixed (**thermite**), in a crucible, and started by a burning magnesium ribbon, interact with great violence:

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe.$$

A temperature of 3000 to 3500° is reached, the molten iron (m.-p. 1530°) collects at the bottom, and the molten aluminium oxide (m.-p. 2050°) floats to the top. Steel rails are welded together *in situ*, and large objects of steel like broken propeller shafts are mended, by enclosing a mass of thermite round the joint and firing it.

557. Aluminium Hydroxide $Al(OH)_3$. The hydroxide is precipitated when ammonium hydroxide, or other alkaline hydroxide, is added to a solution of a salt of aluminium:

$$Al_2(SO_4)_3 + 6NH_4OH \rightarrow 2Al(OH)_3 \downarrow + 3(NH_4)_2SO_4(\text{dslvd.}).$$

It tends to remain in colloidal suspension, and forms a *white gelatinous precipitate*. The mineral bauxite contains a smaller proportion of the elements of water.

Aluminium hydroxide, when *heated*, leaves the oxide:

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \uparrow$$

It is *both weakly basic* and *feebly acidic* in chemical properties. In acids it dissolves forming salts of aluminium, such as the chloride or acetate:

$$Al(OH)_3 + 3HCl \rightleftarrows AlCl_3 + 3H_2O.$$
$$Al(OH)_3 + 3HCO_2CH_3 \rightleftarrows Al(CO_2CH_3)_3 + 3H_2O.$$

These actions are not complete and the salts are hydrolyzed in water (read the equations backwards) giving acid solutions (p. 282). The hydroxide acts also as a feeble acid towards strong bases (see § 558).

Aluminium hydroxide, precipitated from the sulphate, is used with rosin in sizing paper (to fill the capillaries and pores), in purifying water (see § 562), and as a mordant (see § 566) in dyeing. Delicate fabrics (cloth) are rendered waterproof by saturating them with aluminium acetate solution and steaming to promote the hydrolysis. The aluminium hydroxide is precipitated in the capillaries of the cotton or linen, rendering them non-absorbent.

558. Aluminates. Aluminium hydroxide *dissolves* in sodium hydroxide solution, to form **sodium aluminate** Na_3AlO_3:

$$3NaOH + H_3AlO_3 \rightarrow Na_3AlO_3 + 3H_2O$$

and when fused with calcium oxide (or carbonate) it gives calcium aluminate:

Skeleton: $CaO + H_3AlO_3 \rightarrow Ca_3(AlO_3)_2 + H_2O.$
Balanced: $3CaO + 2H_3AlO_3 \rightarrow Ca_3(AlO_3)_2 + 3H_2O.$

The aluminates are hydrolyzed by water, and their solutions have an *alkaline* reaction.

Compounds of aluminium, when heated with a salt of cobalt, leave a *blue* **cobalt aluminate** $(Co)_3(AlO_3)_2$ (test).

559. Aluminium Oxide (Alumina) Al_2O_3. Corundum, and the impure variety **emery,** are next to the diamond in the scale of hardness, and are used as abrasives. **Ruby** and **sapphire** are also crystallized aluminium oxide, containing traces of impurities (chromium in the one case and iron and titanium in the other) to which they owe their colors. By ingenious methods of fusing the oxide, "synthetic" sapphires to the extent of six million carats and rubies to the extent of ten million carats are now made annually. The artificial gems are chemically identical with the natural ones, and can be distinguished only by the fact that they are free from microscopic bubbles and other defects. **Alundum,** an artificial abrasive, and refractory material for crucibles and muffles, is made by barely melting the oxide in the electric furnace.

Aluminium oxide is both basic and acidic.

560. Aluminium Sulphate $Al_2(SO_4)_3,18H_2O$. The sulphate is manufactured by the action of sulphuric acid on bauxite. It crystallizes in leaflets, which usually have a faint yellow tinge due to the presence of iron derived from the mineral. The salt is used in fireproofing cloth, since, when heated, it melts in its water of hydration. It is used as a source for precipitated aluminium hydroxide in paper-making, water purification, and dyeing.

561. Alums. When aluminium sulphate and potassium sulphate are dissolved together in molecular proportions, the solution deposits transparent octahedral (Fig. 30, p. 88) crystals of **potash-alum** K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$. This salt is more easily freed from impurities (*e.g.* compounds of iron) by recrystallization than is aluminium sulphate, and is therefore used instead of the latter in medicine, in dyeing (delicate shades), and to replace the cream of tartar (p. 280) in making baking powder.

Sodium-alum, $Na_2SO_4, Al_2(SO_4)_3, 24H_2O$, **ammonium-alum** $(NH_4)_2SO_4, Al_2(SO_4)_3, 24H_2O$, and also **chrome-alum** $K_2SO_4, Cr_2(SO_4)_3, 24H_2O$ are made in the same way, and crystallize in the same form. The first two are used as sources of aluminium hydroxide, and the last in the "fixing bath" to harden the gelatine on photographic films and plates.

562. Water Purification — Coagulation Process. The suspended matter in water to be used for a domestic supply can be coagulated into larger particles by introducing a small amount of the gelatinous precipitate of aluminium hydroxide. These larger particles, which enclose also the greater part of the bacteria, settle rapidly and the process therefore permits the use of relatively small settling ponds. Aluminium sulphate, made from crude bauxite, and lime are added to the water:

$$3Ca(OH)_2 + Al_2(SO_4)_3 \rightarrow 3CaSO_4 + 2Al(OH)_3.$$

If the water has much temporary hardness, lime is not required:

$$3Ca(HCO_3)_2 + Al_2(SO_4)_3 \rightarrow 3CaSO_4 + 2Al(HCO_3)_3.$$

The carbonate of aluminium, being a salt of *both* a very weak acid and a very weak base, if formed, would be instantly hydrolyzed:

$$Al(HCO_3)_3 + 3H_2O \rightarrow Al(OH)_3 \downarrow + 3H_2CO_3$$

so that aluminium hydroxide is precipitated.

The few remaining bacteria are destroyed by the addition of bleaching powder (p. 235).

Crude ferrous sulphate $FeSO_4$ (copperas), being in many places cheaper (see § 608) than aluminium sulphate, is often used instead of the latter. The lime precipitates ferrous hydroxide $Fe(OH)_2$. This is quickly oxidized to the red ferric hydroxide $Fe(OH)_3$, which coagulates the suspended matter.

563. Clay and Pottery. Pure clay (p. 284) or **kaolin** is white. It is hydrogen-aluminium silicate $HAlSiO_4$. Common clay contains impurities such as sand (silica), limestone, and compounds of iron. Both kinds are plastic when wet and can be moulded. When heated strongly the material shrinks (so that the products are porous) and becomes hard. Bricks, and tiling for roofs and drains, are made of common clay and, when red, owe their color to oxide of iron (Fe_2O_3). The firing is done with fuel gas in ovens or kilns of brickwork. To glaze drain pipes and some bricks, salt is thrown into the kiln. The vapor of the salt produces a more fusible sodium-aluminium silicate, which fills the surface pores. Clay for fire-brick (infusible) must contain free silica, but no lime.

China and porcelain are white, translucent, and non-porous. They are made of pure clay to which a little of the more fusible felspar (p. 284) is added. After firing, the articles are dipped in water, in which the materials for the "glaze," namely finely ground felspar and silica, are suspended. Having thus acquired a thin coating of these substances, they are fired again at a higher temperature and for a longer time. Colored decoration is done with materials which melt (third firing) to colored enamels (p. 275).

Eggshell porcelain contains no clay and is practically a translucent glass.

564. Ultramarine. This material is made by heating together kaolin, sodium carbonate, sulphur, and charcoal, pulverizing the green mass, and heating it again with more sulphur. The product is used as laundry blueing, and in making blue-tinted paper. It is added also to correct the yellow shade of linen, starch, sugar (p. 182), and paper stock.

565. Cement. Cement is made by heating limestone $CaCO_3$, clay and $HAlSiO_4$, or a natural rock containing both materials in the right proportions. Such a rock, made into cement by volcanic heat, was quarried by the Romans near Naples and elsewhere, and its capacity for hardening even under water was utilized by them. The mixture, or pulverized natural rock, is moistened and fed slowly in at the upper end of an inclined (6°) revolving cylinder (20 to 45 by 2 meters). The motion continually turns over the thin layer, and exposes every particle to the heat of the air-blast, charged with pulverized coal, burning in the interior. The product slides out in a continuous stream at the lower end, and is pulverized by steel balls in a ball mill.

Cement is held to be a mixture of calcium silicate and calcium aluminate. The former is simply a filler. The latter is hydrolyzed by the water:

$$Ca_3(AlO_3)_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2H_3AlO_3.$$

The calcium hydroxide slowly crystallizes, connecting the particles of the calcium silicate. The aluminium hydroxide fills the interstices and renders the whole compact and impervious.

Concrete is a mixture of cement with sand and crushed stone or gravel, all made into a paste with water. It sets to a solid mass, suitable for walks, and for the foundations, walls, and floors of buildings. Since no carbon dioxide from the air is required in the hardening process, it sets equally well under water (hence **hydraulic cement**), and is employed in constructing dams, levees, and the foundations of bridges. **Reinforced concrete** contains twisted rods of iron, embedded in the mass, and is much used in building construction. The quantity of cement made in the United States has risen in ten years from 26 million barrels (of 380 pounds) to 80 million barrels (1911).

Blast-furnace slag, when pulverized and heated with limestone, has been found to yield an excellent quality of cement, and a valuable use has thus been found for what was formerly an annoying encumbrance.

566. Dyeing. Cotton and wool are tubular in structure (Fig. 2, p. 2), while silk is a transparent, solid filament. After the dyeing, the color must be, as far as possible, fast to rubbing, light, and washing. When cotton (cellulose, a carbohydrate) is dipped in a solution of most dyes, the latter can be washed out very easily. Wool and silk (proteins, see § 569), on the other hand, are permanently dyed by this treatment. Most dyes are thus "direct" dyes on wool or silk — relatively fewer are so on cotton.

Insoluble Dyes. If the dye is insoluble, and can be *produced* by precipitation *after* the solution has filled the walls and capillary of each fiber of the goods, then it can not afterwards be removed by water. Indigo is of this kind. The cloth is saturated with a solution of indigo white $C_{16}H_{12}N_2O_2$, and the oxygen of the air subsequently oxidizes this and deposits the insoluble indigo blue $C_{16}H_{10}N_2O_2$. Indanthrene blue is applied in the same way as indigo, and is even less affected by light.

Mordant Dyes. Colloidal and gelatinous substances like aluminium hydroxide coagulate and precipitate many dyes, which are themselves colloids. Such a substance is called a **mordant.** The colored precipitate is called a **lake,** and is insoluble. By first saturating the cloth with hot aluminium acetate solution (p. 340) or by using first alum and then ammonium hydroxide, the aluminium hydroxide can be precipitated *within* the fibers of the goods. When the goods are then dyed, the coloring matter is taken up by the mordant, with which it forms an insoluble lake, within the fibers. Aluminium hydroxide forms insoluble lakes with dyes that have no basic properties, such as Alizarin (madder). Chromium hydroxide, iron hydroxide, tin hydroxide, and other gelatinous, insoluble hydroxides of metals are used for the same purpose. For basic dyes, like Malachite green and Methylene blue, tannic acid and insoluble salts of tannic acid (such as antimonyl tannate) are suitable mordants.

Direct Dyes. Many dyes, like Poncean 6R (p. 2), are direct dyes on silk and wool only. Congo-red, no longer much used, and chrysophenin, one of the commonest dyes, dye cotton directly. These dyes, which are sodium salts of organic acids, are colloids and are salted out within the goods by adding sodium sulphate to coagulate them (see soap, § 503), and assist them in forming an insoluble material with the cotton.

567. Exercises.

1. Make equations for the following actions: (1) aluminium on hydrochloric acid; (b) aluminium on mercuric chloride $HgCl_2$; (c) displacement of manganese from manganese dioxide by aluminium.

2. How must aluminium hydroxide be ionized, since it behaves both as an acid and a base?

3. Make the equation for heating calcium carbonate with: (a) aluminium hydroxide; (b) aluminium oxide.

4. Explain why the reaction of a solution of an aluminate is alkaline (p. 282) and that of an alum is acid.

5. Make the equation: (a) for the action of sulphuric acid on bauxite, assuming the formula of the latter to be $Al_2O(OH)_4$; (b) for the formation of potash-alum.

6. Why is the tarnish on aluminium the oxide of the metal, and not the carbonate (as on Zn and Mg)? What qualities in a tarnish enable it to protect the metal from further oxidation (pp. 334 and 338)?

7. Make equations for the action of bicarbonate of soda and aluminium sulphate (alum baking powder) when heated. Explain what raises the bread.

8. Make an equation for the action of: (a) salt on clay at a high temperature; (b) oxygen on indigo white.

CHAPTER XXXVI.

PLANTS, FUELS AND FOOD.

568. Plants and animals are *similar in composition.* They contain much the same *elements*, and these are present in the form of *similar compounds.* They *differ* sharply, however, in the *foods they use in constructing these compounds.* Plants use simple, *inorganic materials;* animals absolutely require complex, *organic substances* as food. The main *chemical processes,* therefore, are *very different* in the two groups. Some of the processes used by plants have been discussed when the substances concerned came up for treatment. We shall here summarize the subject, and complete its outline from the point of view of plant chemistry. This will afford us the basis for understanding the following sections on fertilizers (plant foods), on products of the destructive distillation of vegetable matter, on coal (fossil plants), its uses and products, as well as those on foods, their composition, and digestion in the body.

PLANTS.

569. Plant Composition. We have already learned that plants contain **carbohydrates** (cellulose, starch, and sugars, Chap. XIX) in large amounts, and **esters** (vegetable oils, p. 300) in smaller quantities.

The **proteins** are contained very largely in the fruits, and also in the protoplasm which is found in every cell. Thus, gluten, a mixture of two proteins, accompanies the starch (p. 180), and constitutes about 10 per cent of wheat flour. In peanuts the percentage of proteins is 26, while in leaves, stems and roots, the moisture is very high, and the proteins much lower (lettuce 1.2, potatoes 0.9, turnips 1.3).

The proteins are white, amorphous substances which differ from the carbohydrates and esters in that, besides carbon, hydrogen, and oxygen, they contain, on an average, 16 per cent of *nitrogen*, 1 per cent of *sulphur*, and in many cases, *iron* or *phosphorus* as well.

Plants contain, also, compounds of *potassium*, *magnesium*, and *calcium*.

Individual plants are noted for containing *special compounds*. **Alkaloids,** like quinine from the bark of the cinchona, morphine from the seed capsules of the opium poppy, strychnine from the seeds of *nux vomica*, are used in medicine. Caffeine gives their stimulating qualities to the extracts from the leaves of tea and the beans of coffee. The *laurus camphora* of Formosa is our chief source of **camphor.** Until recently, twenty-five million dollars worth of indigo (§ 566) was extracted from the *Indigofera tinctoria* in India alone, although now most of this dye is made from naphthalene ("moth-balls"). There are hundreds of valuable substances each of which is thus found in only one or at most in a very few species of plants.

570. Plant Nutrition. As we watch the growth of a seedling from day to day, we say it " comes up out of the soil." But it does *not*, entirely — the solid part of it *comes mostly out of the air*. The cellulose, starch, and sugar owe their carbon to **carbon dioxide** absorbed through the leaves (p. 165). The **water** (90 to 95 per cent of the whole weight) does indeed come from the soil, as do the nitrogen and sulphur, and the phosphorus and iron required for forming the proteins. The potassium, magnesium, and calcium also ascend with the sap. But the carbohydrates are never less in amount than all the other components together (except the water), and are often ten times greater.

571. Fertilizers. The soil is always able to supply the necessary amounts of magnesium, calcium, and iron (as bicarbonates). But it may lack sulphur (as sulphates), nitrogen (absorbed chiefly as nitrates), potassium (as sulphate, chloride or nitrate), and phosphorus (as soluble phosphates). The soil may have been originally deficient in one or more of these necessary plant foods, or the supply may have been exhausted by repeated cropping. Every crop removes permanently a certain part of the supply. Thus, in the case of nitrogen, each crop of maize (corn, 45 bushels) removes 63 pounds per acre, a crop of cabbage (15 tons) removes 100 pounds per acre, clover hay (2 tons) 82 pounds, and wheat (15 bushels) 31 pounds. When the supply becomes reduced, the crops become poor. Moreover, the elements must be in *soluble form* (p. 265). Felspar and calcium phosphate $Ca_3(PO_4)_2$ are not changed by weathering into soluble salts of potash and soluble phosphates with sufficient speed to meet the annual demands (p. 284).

It is just as necessary to feed crops as to feed cattle, and equally foolish to starve either of them. Fertilizers are used to make good the original, or acquired deficiencies. **Potassium salts,** chiefly from Stassfurt (p. 284), furnish the potash. **Superphosphate of lime** (p. 265) supplies the phosphate.

572. Fertilizers — Nitrogen. The **nitrogen** is applied as sodium nitrate (p. 282), calcium nitrate (p. 247), ammonium sulphate (pp. 200 to 201), calcium cyanamide (p. 327), manure (pp. 284, 357) or the offal ("tankage") and ground bones from slaughter houses. Most plants probably do not utilize compounds of ammonium, as such. The ammonium salts are first oxidized by the help of nitrifying bacteria in the soil (p. 284) to give nitric acid, which, with the lime, gives calcium nitrate.

Over every acre of the earth's surface there are 34,000 tons of free nitrogen. Until recently it was supposed that none of this immense store was ever used by plants. It has now been found, however, that peas, beans, clover, alfalfa, and other plants of the order *leguminosæ*, bear round their roots colonies of a kind of bacteria which has the power to bring free nitrogen into combination. In these root nodules (Fig. 86) the bacteria first produce proteins, which later decompose and ultimately, by bacterial action, yield nitric acid. In this way a crop of clover will fertilize the soil, not only for itself, but also for the following crop. One advantage of the rotation of crops is therefore at length explained.

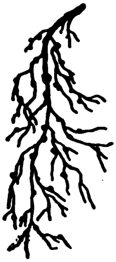


Fig. 86

The value of the systematic use of fertilizers is indicated by comparison of the average crop of wheat per acre in different countries. The average of ten successive years is: Denmark 40 bushels, Great Britain 33, Germany 29, United States 14.

Fuels.

573. Destructive Distillation of Wood. When dry wood is heated in iron retorts the compounds which it contains (p. 347) are decomposed. Much of the carbon remains in the form of **charcoal**. The vapors which pass off (through the pipe on the right, Fig. 87) deposit, when cooled, much **liquid material**. The uncondensed **gases** are combustible and are used for heating the retorts

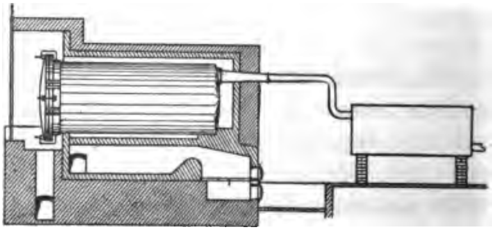


Fig. 87

or other similar purposes. Hard wood furnishes, approximately, 25 per cent of its weight of charcoal, 25 per cent of gases, and 50 per cent of liquids. The liquid contains acetic acid (10 per cent, uses, pp. 186, 340, 384), methyl alcohol CH_3OH or wood spirit (3 per cent, uses, p. 186), a complex, tarry mixture, used in road-making (10 per cent), water (77 per cent), and a little acetone (uses, pp. 171, 312). The gases contain a large part of the nitrogen of the original proteins in the form of ammonia (uses, p. 205), which is dissolved out with water.

In the old method, still practised, the wood was stacked, covered with turf (Fig. 88), and set on fire. A part was burned, the rest was turned into charcoal, and all the valuable volatile products were lost.

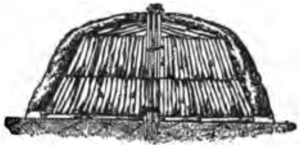


Fig. 88

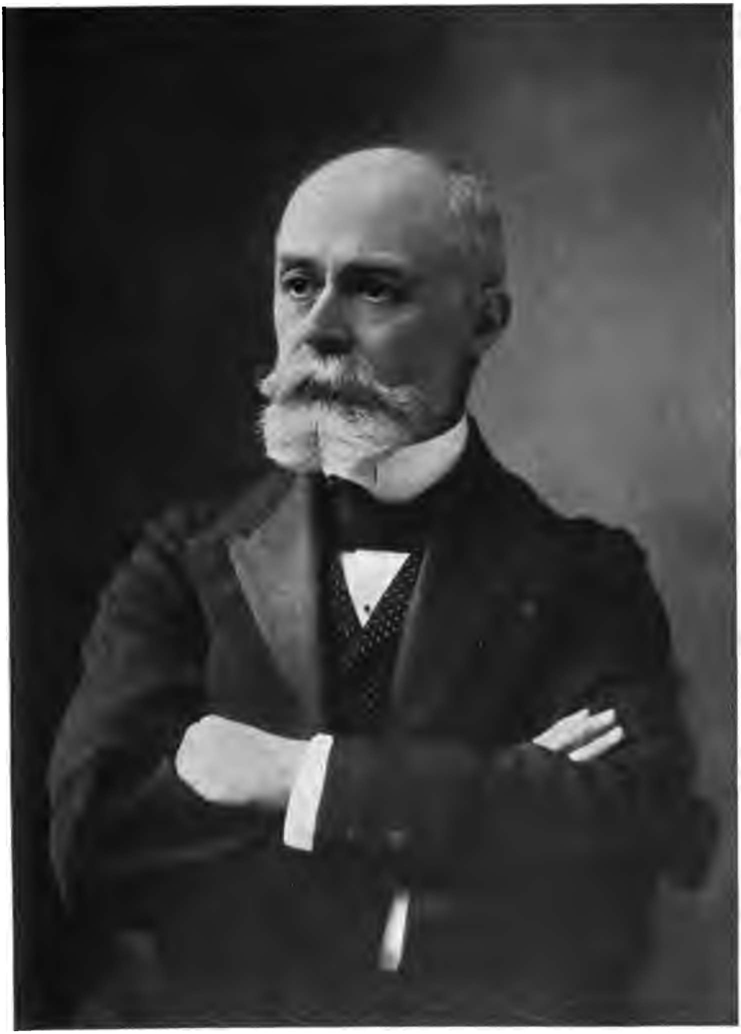
574. Properties of Wood Charcoal. The charcoal retains the structure — a complex network of minute cells — of the original wood, and therefore has a *surface* which is vast in proportion to the amount of material it contains. For this reason it will take up many times its own volume of gases, especially the more condensible ones (p. 97). Thus, boxwood charcoal takes up ammonia (90 volumes), hydrogen sulphide (55 volumes), and oxygen (9 volumes). For the same reason, when pulverized and shaken with a liquid, it extracts dissolved materials such as dyes (indigo, cochineal, litmus, etc.) and coloring matters (see sugar refining, p. 182), especially those of a colloidal nature. Charcoal is used, also, in making gunpowder, in reducing ores, and as a fuel (smokeless).

575. Coal. When wood burns with a plentiful supply of oxygen, it gives nothing but carbon dioxide, water, free nitrogen, and a certain amount of ash (oxides and carbonates of the metals). What happens when it is heated in absence of oxygen, we have just seen. In nature, however, the intermediate case, of slow decomposition of vegetable matter, *without* much heating and *without* access of oxygen, takes place on a large scale. Clay and sand, or even simply water, cover the vegetation and exclude the air, and the products are anthracite coal, bituminous coal, or peat. Little is known of the actual compounds contained in coal. We are concerned mainly with the products obtained by heating it in the absence of air, and with its use as a fuel.

576. Coal Analysis. The *moisture* is measured by heating 1 g. at 105° for 1 hour. Much water lowers the fuel value, because of the heat wasted in vaporizing it. After reweighing, the sample is heated with a Bunsen flame in a covered crucible to drive off the *volatile matter*. After weighing again, the air is admitted and strong heat applied to burn up the *fixed carbon* (coke). The remainder is the ash. For example:

	Water.	Volatile matter.	Fixed C.	Ash.	Sulphur.
Bituminous I........	1.3	36.7	53.5	8.5	1.7
Bituminous II.......	0.7	17.9	75.8	5.6	1.2
Anthracite...........	3.0	5.6	80.5	10.9	0.8

Bituminous coals give much, and widely varying amounts of volatile matter; anthracite coals give very little. The ash is the mineral matter of the original plants, with additional rock materials in some specimens. The coal is selected according to the purpose for which it is to be used. For coal gas, and even for coke, a variety high in volatile matter is chosen. For water gas (p. 163) anthracite or coke itself is employed.



HENRI BECQUEREL
French physicist. Discoverer of radioactivity, 1852–1908

577. Coal Gas. The gas plant (Fig. 89) includes: (1) the fire-brick retorts in which the coal is heated (externally) to 1300°, (2) the hydraulic main (a wide iron pipe) immediately above them in which most of the tar collects, (3) the condenser and wash box for cooling, condensing, and removing oils, (4) the scrubbers (vertical and rotary) where the ammonia is taken out by water dripping over strips of wood and by stirring the gas with water, (5) the purifier where hydrogen sulphide is taken up by hydrated ferric oxide, and (6) the holder in which the gas collects.

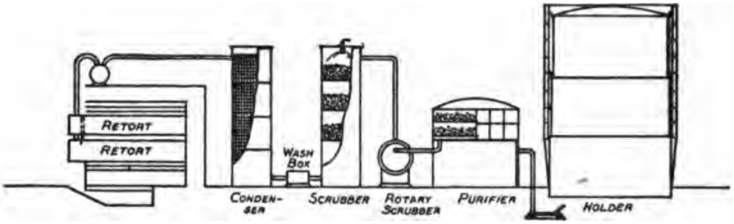


Fig. 89

One short ton (2000 lbs.) of the bituminous coal I (in above table) gave: *Gas* 10,500 cubic feet with 13 candle power,* *coke* 1325 pounds, *ammonia* 5 pounds (equal to 20 pounds $(NH_4)_2SO_4$, worth $60 per ton †), and *tar* 12 gallons. The percentages of the various *components of the gas* were: Illuminants (C_2H_4 and C_6H_6) 3.8, CO 8.7, H_2 50.5, CH_4 28.2, C_2H_6 2.8, CO_2 2.1, O_2 0.4, N_2 3.5. Calorific power (see § 581), 610 B.T.U. per cubic foot. Specific gravity (air = 1) 0.43.

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* Flame burning 5 cu. ft. per hour.

† Garbage (after the extracting of fats, which can be made into soap), when subjected to destructive distillation, yields, amongst other valuable products, no less than 70 to 85 pounds of ammonium sulphate per ton. At present, as a rule, much money is actually *spent* on throwing these materials away.

578. By-products. Often the retorts can be opened at both ends, so that the coke may be pushed out by a ram. Frequently they are vertical, so that the charge can be run in, and the coke afterwards removed by gravity. They hold 1000 to 1700 pounds of coal per charge.

The ammonia is made into ammonium sulphate. The tar may be used for road-making, as a waterproof material in building, and wherever pitch is applicable. Frequently it is separated by distillation, and other forms of treatment, and yields benzene C_6H_6 (for aniline and many dyes and drugs), naphthalene $C_{10}H_8$ (moth-balls, and starting point for synthetic indigo and for Congo red), anthracene $C_{14}H_{10}$ (from which alizarin and indanthrene are made), phenol or carbolic acid C_6H_5OH (§ 517), and other valuable substances.

Water gas (p. 163) and carburetted water gas (p. 173) have been discussed already.

579. Coke Ovens. The **by-product coke oven** is very much like the plant used for making coal gas. The difference is that the heating is arranged so as to decompose the volatile matter and cause it to leave as much as possible of its carbon behind (p. 173). The resulting gas is consequently poor in illuminants, but excellent as a fuel. The ammonia and tar are also diminished in amount, but are still produced in paying quantities.

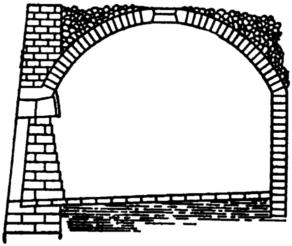

Fig. 90

The **beehive** coke oven (Fig. 90) is a primitive device of firebrick, shaped like a beehive. It is simply filled with coal, part of which is allowed to burn with a limited supply of air. It yields 66 per cent coke, against 73 per cent from the by-product oven. All the volatile matter, with its gas, ammonia, and tar, escapes through an opening at the top, where it burns in a large flame and is wasted. (For the relative numbers of the two kinds of ovens, see p. 200.)

580. Properties and Uses of Coke. Coke is a grey-black, hard material of spongy texture. It burns without flame, and gives a higher temperature than does coal, because no heat is used in vaporizing moisture and volatile matter. On account of these and other properties, it is used in immense quantities in reducing ores of iron and other metals, and in smaller amounts in electric furnace work and in making electric light carbons.

581. Coal as Fuel. The quality of a fuel coal, and whether it is worth its price, is learned by measuring its **calorific** (heating) **power.** A sample (about 1 g.) is burned in a **bomb calorimeter.** This is a closed, metal vessel, filled with compressed oxygen and submerged in a known weight of water. The coal is set on fire by a wire heated electrically and, after it has burned, the increase in temperature of the water is read off. The heat of combustion is the heat in calories (p. 50) evolved by the burning of 1 g. of coal. In engineering practice they use the number of British Thermal Units (1 B.T.U. = heat required to raise 1 pound of water 1° F.) developed by 1 pound of coal, and call the result the calorific power.

	Calories per 1 g.	B.T.U. per 1 lb.		Calories per 1 g.	B.T.U. per 1 lb.
Hydrogen........	28,800	51,840	Coal...........	7,800	14,040
Charcoal (to CO_2)...	8,080	14,544	Anthracite......	8,000	14,400
Wood (seasoned).....	4,750	8,550	Petroleum......	11,000	19,800

Knowing that 100 cal. will raise 1 g. of water from 0° C. to 100° C., and 540 cal. more will convert it into steam, it is possible to calculate how much steam should be furnished by 100 kilog. of coal of known heat of combustion. If the quantity falls short, then the furnace, draft, or method of firing may be defective. Too much draft, for example, merely introduces additional, useless material (air) to be heated. Thus, if the flue gas, upon analysis, is found to contain, not 12 per cent carbon dioxide (normal), but only 3 per cent, then for every ton of coal burned, 52 tons of unnecessary air have been raised to the temperature of the furnace. By chemical tests, made in ways like this, the efficiency of every device in the modern factory is (or ought to be) controlled. If the coal is bought without heed to its calorific value, and used without experimental checks, the boiler house alone may easily waste the whole profit earned by the rest of the plant.

FOOD.

582. Composition of the Human Body. The following gives, roughly, the percentage of each element in the human body.

O.......65	N..........3	K.......0.35	Cl.......0.15	I...trace
C.......18	Ca.........2	S.........0.25	Mg......0.05	F..trace
H.......10	P..........1	Na......0.15	Fe.......0.004	Si..trace

We have already learned that the calcium and phosphorus are chiefly in the bones (p. 261). The nitrogen, sulphur, and iron are in the proteins. The sodium is largely present as salts, in the fluids of the body. The potassium is in the soft tissues and in special secretions like milk. As in the plant, the carbon, hydrogen, and oxygen are in the form of carbohydrates, proteins, and fats, and there is also much water.

583. Elimination. Certain amounts of all these elements leave the system daily. Water evaporates from the lungs and skin. The carbon leaves in large amounts, chiefly from the lungs as carbon dioxide, and also as excreted fats, proteins, and carbohydrates. Much of the nitrogen is eliminated, chiefly as urea $CO(NH_2)_2$. The salts are removed in the same way.

During the decay of manure, the urea is hydrolyzed, to form carbonic acid and ammonia. The odor of the latter is easily recognizable:

$$CO(NH_2)_2 + 2H_2O \rightarrow H_2CO_3 + 2NH_3.$$

584. Animal Nutrition. Since there is continual loss, there must be continual replacement. The animal can use, for the most part, only complex compounds (p. 347). It resembles the plant, in the fact that it can take up into its system *only dissolved material.* It differs from the plant, however, in the fact that it is provided with a wonderful laboratory in which insoluble substances are changed into soluble ones. This is the *digestive tract,* consisting of the mouth, stomach, and intestine. The production of soluble substances of suitable composition is called *digestion.*

The *processes* are too complex for detailed treatment here. Only a few typical *illustrations* can be given. The *principles* concerned have all been used and illustrated already, and many of the facts are contained in previous chapters.

585. Foods. First, let us examine the table showing the percentage composition of the edible portion of several articles of food:

Food material.	Water.	Protein.	Fat.	Carbohydrate.	Ash.
Beef (lean)	73.8	22.1	2.9	....	1.2
Cod	82.6	15.8	0.4	....	1.2
Eggs	73.7	14.8	10.5	....	1.0
Milk*	87.0	3.3	4.0	5.0	0.7
Butter	11.0	1.0	85.0	....	3.0
Cheese (cheddar)	27.4	27.7	36.8	4.1	4.0
Oatmeal	7.3	16.1	7.2	67.5	1.9
Wheat flour	11.9	13.3	1.5	72.7	0.6
Beans (dried)	12.6	22.5	1.8	59.6	3.5
Almonds	4.8	21.0	54.9	17.3	2.0
Maize (green corn)	75.4	3.1	1.1	19.7	0.7
Potatoes	78.3	2.2	0.1	18.4	1.0
Lettuce	94.7	1.2	0.3	2.9	0.9

* The emulsified fat separates slowly as the cream; the protein (casein, colloidally suspended in the skim milk) is coagulated by rennet and constitutes cheese; the carbohydrate (lactose, a sugar) is then left in the water, along with inorganic salts.

We note, at once, that there is little more water in milk than in cod; that the animal foods, except milk (carrying lactose, p. 181), contain no carbohydrates; that potatoes and corn when dried are nearly all carbohydrate (starch); that lean beef when dry is nearly all protein; that some seeds (wheat and beans) contain almost no fat, some (oats) much more, and some (almonds and nuts) a very large amount; and that lettuce and other leaves are mainly water, with dissolved inorganic salts (valuable), contained in a light framework of cellulose (non-digestible).

586. Digestion of Starch. The carbohydrates, in most foods which contain a large proportion of them, are mainly in the form of starch. The exceptions are milk, sweet fruits, and sugar itself. Starch is insoluble in water, and therefore can not be absorbed. We have seen (p. 180) that, when boiled with a dilute acid, it is hydrolyzed, giving glucose. When bread and potatoes are masticated, an enzyme (organic catalyst), named **ptyalin,** contained in the saliva (alkaline) turns a part of it, by hydrolysis, into a soluble sugar, maltose. Later, in the small intestine, **amylopsin** completes this process. Here also another enzyme, **maltase,** splits the maltose into glucose. The glucose then passes through the intestinal wall and so goes into the circulation, where most of it is oxidized.

The *cooking of* starch (*baked* bread, *boiled* potatoes, etc.), breaks up the grains (p. 180), and makes the mixing with the enzyme more perfect and the digestion more rapid and complete.

587. Digestion of Fats. Fats, if already emulsified, as in milk, are hydrolyzed by a **lipase** (enzyme for *fat*) in the gastric juice of the stomach, and are decomposed into the acid and glycerine (p. 302). Fat in larger masses is hydrolyzed by lipases in the bile and here the acid (insoluble in water) is dissolved. The acid and the glycerine then diffuse through the intestinal wall and finally recombine to form fat in the blood. Some of this fat is deposited in the tissues and some is oxidized (giving muscular energy and heat).

Cooking (application of heat) does not affect the digestibility of fat. However, when fat is heated too strongly, the beginning of destructive distillation produces unsaturated compounds. These are intensely irritating to the digestive organs — as the way their vapors bring tears to the eyes would lead us to expect.

588. Digestion of Proteins. The proteins, of which the white of an egg (albumen) is a typical example, are not affected by saliva, but, when mixed with the gastric juice of the stomach, they are changed by the free hydrochloric acid it contains into **syntonin.** This in turn is hydrolyzed by the **pepsin** (enzyme), also contained in the gastric juice, into **peptones** which are soluble in water. These changes, only partly carried out in the stomach, are completed in the small intestine by the **trypsin** of the pancreatic juice, and the peptones (or amino-acids into which they are split) pass through the intestinal wall into the circulation. The **casein** of milk, being in colloidal suspension, is completely hydrolyzed to peptones in the stomach.

When heated, as in *cooking*, the proteins do not behave alike. Some, like albumen (white of egg) become coagulated, though probably *not* less digestible. The same is true of the blood proteins (hæmoglobin, etc.) of beef. On the other hand, the connective tissue of meat (chiefly **collagen**) is insoluble in cold water, but in hot water goes into colloidal suspension as **gelatine**. It is therefore softened by judicious roasting (under-done meat), provided the operation is not carried so far (over-done meat) that the water in the meat is largely evaporated.

589. Fuel Value. While the food is needed to replace the material which is continually eliminated from the system, the organism also requires energy to maintain the routine motions of the heart, intestines, lungs, and other organs, and the normal muscular tension, as well as the movements of the muscles in walking and working. If the heat derived from routine changes is not sufficient to maintain the temperature (39° C.) of the body, then additional material is oxidized by the system for this specific purpose. The values of foods are therefore conveniently estimated in terms of the heat they produce when burned — their **fuel values.**

The average fuel values, as measured in the calorimeter, with certain necessary corrections, and expressed, as is usual in this work, in **large calories** * *per gram*, are: Carbohydrates 4 Cal., fats 9 Cal., proteins 4 Cal. The fuel values *per pound*

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* One large calorie (1 Cal.) is equal to one thousand small calories (1000 cal.), as hitherto defined (p. 50) and used.

[illegible] 89-90-91

(= 453.6 g.) are 453.6 times greater: Carbohydrates 1800 Cal., fats 4080 Cal., proteins 1800 Cal.

590. Normal Diet. There is much uncertainty, as yet, in regard to the best choice of foods, in respect to the exact distribution in kind and quantity. We know, however, that life cannot be maintained on one kind (say, gelatine) alone. A mixed diet is necessary. In general, it appears that 100 g. of proteins (giving 4 × 100 Cal.) per day, and a sufficient amount of other foods to bring the total fuel value up to 2200 Cal. per day, is enough for a person leading a strictly sedentary life. For work involving physical exercise, larger values, up to about 3800 Cal., are required.

From the data given in the table (p. 358) the fuel value of 100 g. of each kind of food can easily be calculated.

591. Fuel Values and Prices of Foods. If the current prices are considered, one can also readily calculate the fuel value obtainable for a given sum of money invested in each kind of food. Thus; lean beefsteak contains 22.1 per cent of protein (p. 358), or 0.221 pounds per pound of meat. The fuel value of this protein is 0.221 × 1800, or 398 Cal. per pound.

	Price * per 1 pound, cents.	Fuel values per 1 lb.				Cal. per 10 cents.
		Protein	Fat.	Carbohyd.	Total.	
Steak	25	398	118	....	516	206
Eggs	24	266	428	....	694	290
Oatmeal	5	290	294	1215	1799	3600
Flour	5	249	61	1309	1619	3240
Almonds	40	378	2240	311	2929	732
Potatoes	2.5	40	4	331	375	1500
Cheese	25	500	1500	74	2074	830

* The prices vary greatly with the quality, the season of the year, the demand, the supply, etc.

592. Animal Charcoal. When bones or dried blood are subjected to destructive distillation, gases and vapors are given off and charcoal remains. The charcoal from bones (**bone black**) contains 90 per cent of mineral matter (largely $Ca_3(PO_4)_2$) and only 10 per cent of carbon. Both kinds of animal charcoal, being very active as decolorizers, are used in sugar refining.

593. Exercises.

1. Give the uses of: (a) acetic acid; (b) methyl alcohol; (c) acetone; (d) each form of carbon mentioned in this chapter or elsewhere in the book.

2. (a) Why are charcoal and coke smokeless fuels? (b) Explain why bituminous coal burns with flames while anthracite does not.

3. In making charcoal, why is the turf used?

4. Point out the analogies between the processes used in making coke and charcoal, and between their properties and uses.

5. What gas is given off when vegetable matter decomposes under water (p. 171)?

6. What compounds, contained in the original plants, furnish: (a) the hydrogen sulphide; (b) the ammonia obtained on distilling coal?

7. A gas of sp. gr. 0.43 (air = 1) gives, on burning, 610 B.T.U. per cu. ft. How many B.T.U. is this per pound?

8. How many kilog. of steam can be made by burning 100 kilog. of coal, the heat of combustion of which is 8500 cal.?

9. How many pounds weight of steam can be made by burning 50 lbs. of coal of calorific power 14,500 B.T.U.?

10. At 5 atmos. pressure and 152° C., how many cubic meters will 190 kilog. of steam occupy?

11. Find the shortest method to prove that the calorific power is always numerically 1.8 times the heat of combustion (p. 355).

12. What is "conservation"? What four industries or operations (or ways of performing operations) that are *wasteful* have been mentioned in this chapter (compare pp. 200 and 201)?

13. Rewrite the statement on p. 356, lines 1–4, in terms of B.T.U., degrees F. and pounds.

14. By what changes does stable manure furnish food for plants?

15. Make equations for the formation: (a) of maltose from starch; (b) of glucose from maltose.

16. Make a connected statement showing the stages in the digestion of milk.

17. If we regard the hæmoglobin in the red blood-corpuscles as a catalyst (p. 26), what actions does it catalyze?

18. Why does fat appropriately form a larger proportion of the diet in the Arctic regions than elsewhere?

19. Give the weights of carbohydrate, protein, and fat which would supply a menu, such that the total food value was 3000 Cal., and that 100 g. of protein was included, and the remaining fuel value was divided equally between carbohydrates and fats.

20. Calculate the fuel value of 1 kilog. of: (a) wheat flour; (b) oatmeal; (c) lean beef.

CHAPTER XXXVII.

IRON, NICKEL, COBALT.

594. Having disposed of most of those metallic elements, the chemistry of which, because of the fact that each has only one valence, is comparatively simple, we turn now to the metal which is by far the most important of all in the industrial standpoint, namely iron.

IRON Fe.

595. Occurrence. Particles of free iron are found in igneous rocks, and larger pieces in meteorites. Compounds of iron are very widely distributed, in the soil and rocks (giving yellow and red tints), in the chlorophyl and proteins of plants and in the hæmoglobin and other proteins of animals. Pyrite FeS_2 (fools' gold) is used mainly as a source of sulphur for sulphuric acid. The ores which yield iron itself are:

Fe_2O_3 (ferric oxide), **red hæmatite.** Red when pulverized.
$2Fe_2O_3,3H_2O$ (hydrated ferric oxide), **brown hæmatite.**
Fe_3O_4 (magnetic oxide of iron), **magnetite.** Black when pulverized.
$FeCO_3$ (ferrous carbonate), **spathic iron ore.**

The carbonate, mixed with clay (clay iron-stone), furnishes most of the iron in Great Britain, but less than one per cent of it in the United States. The ore is first calcined to produce the oxide.

596. The Blast Furnace. *Coke* is used to reduce the oxides and as fuel. The carbon monoxide CO, produced by the burning of the coke and air, is the actual reducing agent:

$$Fe_2O_3 + 3CO \rightleftarrows 2Fe(\text{melted}) + 3CO_2 \uparrow$$

Since, however, the ores contain rocky material (gangue), such as silica SiO_2 and silicates of aluminium, *limestone* is added in the proportion required to give a fusible slag (p. 272). Thus the whole material is converted into gases which ascend, and liquids (melted iron and slag) which flow down.

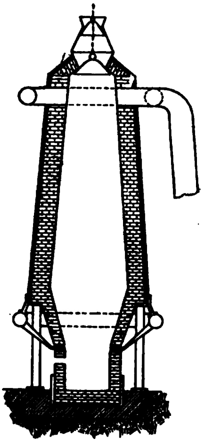

Fig. 91

The blast furnace (Fig. 91) is an iron structure 40 to 100 feet high, lined with fire-brick. A circular pipe delivers compressed air to several nozzles (tuyeres). The ore, coke, and limestone are admitted from the hopper at the top by lowering two bells, only one of which is opened at a time. The gases escape at openings below the bells into the downcomers. The highest temperatures are reached, and the most chemical action occurs, at the widest part. The melted iron and slag (immiscible) collect in two layers in the hearth or crucible at the bottom. From time to time the slag is allowed to flow from an opening near the top of the crucible, and the iron from a similar opening at the bottom and 90° from the former. Plugs of wet clay close the openings and are instantly baked hard. The iron is taken in ladles to other parts of the plant, or is cast into "pigs" in steel moulds and chilled in water. When the proportions of the material are properly controlled by analyses, the furnace runs continuously until the lining is worn out.

597. Reactions in the Blast Furnace. The action (see equation, above) is a *reversible* one and the carbon dioxide formed reacts with the iron to reproduce the original materials. The system reaches equilibrium when about 1 volume of carbon dioxide is present with 1½ volumes of carbon monoxide. To keep the action going *forward* there must, therefore, be constantly present an excess of carbon monoxide beyond this amount, namely about 2 vols. CO : 1 vol. CO_2. This means that the gases *issuing at the top* contain the same *proportions*, or about 20 per cent CO, 10 per cent CO_2, 70 per cent N_2.

The downcomer gas is therefore combustible, and is used in the blowing engines, and for heating the air-blast to 400 to 550°. From 3 to 4 tons of air are required for every ton of iron produced. The moisture in this air acts upon the coke, giving water gas (p. 163). This uses up fuel, and also lowers the temperature just where it ought to be highest. In the most modern furnaces, therefore, the air is dried (Gayley dry-blast process) with a saving of $1.00 per ton of iron. In 1911, 23,250,000 tons of iron were produced in the United States.

598. Cast Iron. Pig iron contains 4 to 5 per cent of carbon and varying amounts of silicon (as silicide of iron), phosphorus (as phosphide) and sulphur (as sulphide). These impurities lower the melting-point from 1510° to about 1100°. The material is hard and brittle. Most of it is made into wrought iron or steel, but some is used in making objects of cast iron, such as ranges, stoves, pipes, and radiators, which are not to be subjected to shocks or strains. Cast iron expands on solidifying and forces itself into the details of the mould.

By adding pyrolusite MnO_2 in the blast furnace, cast iron containing from 20 per cent of manganese (spiegeleisen) up to

80 per cent (ferromanganese), and carbon up to 6 per cent, is made for use in steel manufacture.

599. Wrought Iron. Wrought iron is commercially pure iron. The broken pigs are placed in a **reverberatory furnace** (Fig. 92), the hearth of which is covered with a bed of hæmatite ore Fe_2O_3 and silicates. The flames and heated gases, deflected by the low roof, play upon the iron and melt it. The oxygen in the hæmatite combines with the carbon, phosphorus, sulphur, and silicon, giving the oxides. The mass is worked vigorously with iron rods upon the bed of hæmatite (puddled), carbon monoxide escapes, and the iron becomes more viscous as its melting-point rises on account of the removal of the impurities. Finally, it is collected in balls (blooms) on the iron rods. The treatment occupies an hour and a half. To press out the slag, the blooms are first passed through a squeezer and then put through the rolls. The resulting bars are repeatedly cut, "piled" in a bundle, reheated, and rolled. This treatment, and the presence of a little slag distributed through the mass, give wrought iron the valuable *properties* which distinguish it from all other iron products, namely its *fibrous fracture* and its extreme *toughness.* On account of these properties it is used for anchors, chains, and bolts. It is drawn into wire, and, when heated, can be cut, shaped, and

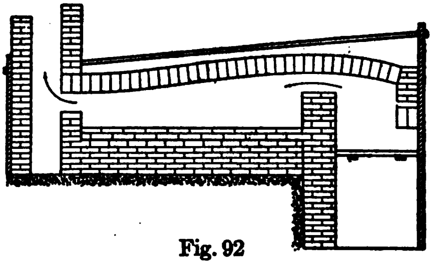

Fig. 92

welded under the hammer. The impurities having been greatly reduced (to 0.1 or 0.2 per cent), this iron is much *less fusible* than cast iron, and is used for fire bars.

600. Crucible Steel. Steel contains 0.75 to 1.5 per cent of carbon, and is freed as far as possible from other impurities. Small lots, for special purposes, are made in clay (or graphite and clay) crucibles in melts of 60 to 100 pounds. The charge in Sheffield consists of blister steel, *i.e.* carburized Swedish wrought iron of varying carbon content. The modern method is to melt " melting bar," a very pure open hearth steel with charcoal, or even pure pig iron. Crucible steel is used in making razors (1.5 per cent C), tools (1 per cent C), dies (0.75 per cent C), pens, needles, and cutlery.

Electric heating (*e.g.* in the Heroult furnace), recently introduced, permits the steel maker, first to wash the molten iron with basic slags of high oxidizing power until perfectly pure, and then by suitable additions to give it any required final composition.

601. Properties of Steel. Cast iron can be melted and cast, is hard when chilled, but can not be forged or rolled. Wrought iron is slagbearing and *malleable*, and is not hardened by quenching from a high temperature. It is never cast. Steel is free from slag, being cast from an originally liquid condition. If its carbon content is high enough, it can be *hardened* by quenching. Steel has also greater *tensile strength** than wrought iron, which increases with the carbon content, and it can be *permanently magnetized.* In addition, high carbon steel can also be *tempered* (§ 602) to the required degree of hardness.

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* **Tensile strength** or **tenacity** is measured by the weight (in kilograms) required to break a wire of the metal 1 sq. mm. in section. Lead 2.6, copper 51, iron 71, steel 91.

602. Tempering. To understand the tempering, it must be noted that the carbon in steel is in the form of carbon or of a carbide of iron Fe_3C (6.6 per cent C) homogeneously dissolved in the iron. When white hot steel (up to 2 per cent C) is *suddenly chilled*, there is no time for any changes to occur during the cooling, and a *solid solution* is obtained which is very hard and brittle. When, however, the cooling is slow, some of the carbon separates in minute crystals of cementite, carbide of iron Fe_3C, until at about 700° there remains only 0.9 per cent of carbon in solution. At this temperature the solid solution breaks down into a mechanical mixture of pure iron which is soft, and carbide of iron which is hard. Steel is thus a mixture, and not homogeneous, when slowly cooled. When therefore hard, chilled steel is heated once more for the purpose of tempering, the extent to which the softer material is formed depends on the temperature reached, and on the rate and duration of the cooling permitted. By varying these the degree of hardness allowed to remain can be adjusted.

Phosphide of iron makes steel brittle when cold ("cold short"). Sulphide of iron makes it brittle when hot ("red short"), and unsuitable for forging. Hence phosphorus and sulphur are reduced to the lowest possible amounts.

603. Bessemer Process. Pig iron is melted and run into the converter (Fig. 93), which is lined with firebrick, measures about 15 by 8 feet, and holds 15 tons. An air-blast, entering through one axle, blows through the metal from tuyeres at the bottom. The oxidation of the carbon and silicon, which raises the temperature above the melting-point of pure iron, is over in 20 minutes. Spiegeleisen is then added to give the

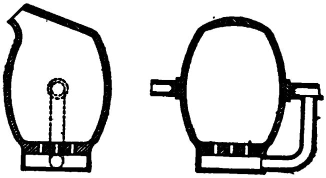


Fig. 93

desired percentage of carbon and manganese, and the liquids, first the slag and then the iron, are poured into ladles, and the metal is cast.

Sulphur and phosphorus are not removed by the air. If present in too great amounts, they are removed by lining the converter with basic material such as magnesium and calcium carbonates (Thomas-Gilchrist process). The slag then contains phosphates, and is valuable as a fertilizer.

Bessemer steel is used for heavy and light machinery castings, and is rolled into bridge and structural iron. It contains from 0.1 per cent (soft) to 1 per cent (hard) of carbon.

604. Open-hearth (Siemens-Martin) Process. In this process pig iron and scrap iron (up to 75 tons) are melted on a hearth lined with firebrick and sand (Fig. 94). At a later stage hæmatite is added to furnish oxygen (as in puddling). To secure economically the temperature necessary to keep the

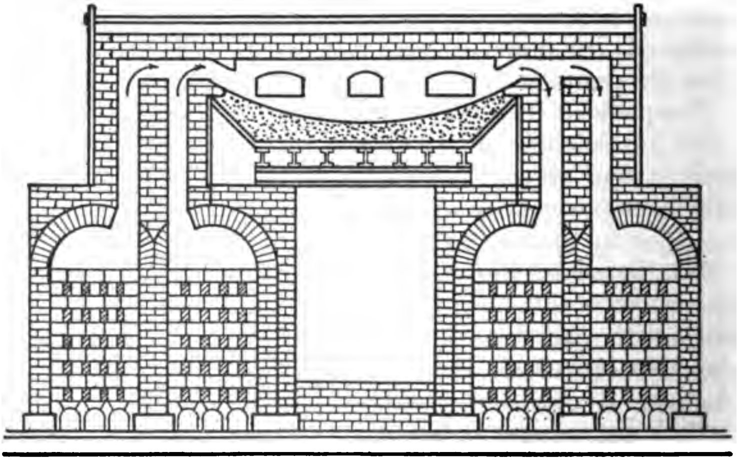


Fig. 94

pure product (iron) fused, Siemens contributed the idea of *preheating* the fuel gas and air by a *regenerative* device. The spent air and gas pass down through a checker work of brick. When this has become hot, the valves are reversed, the gas and air now enter through the hot brick work and pass out through the checker work on the opposite side, raising its temperature. The direction of the gases is changed every twenty minutes or so, and the whole operation lasts 8 to 12 hours.

During casting some aluminium is added to combine with oxygen (present as CO) and so give sounder ingots. Recently, iron containing 10 to 15 per cent of **titanium** has been added instead. The titanium combines with both nitrogen and oxygen, and passes into the slag. Rails made of steel purified with this element are less liable to breakage and are 40 per cent more durable than ordinary open-hearth rails. There are nearly a million tons of these rails now (1912) in use in the United States.

The advantage of this process over that of Bessemer is that it is not hurried and is therefore under better control. The material can be tested by sample at intervals, and defects corrected. The product is of better and more uniform quality.

As in the Bessemer process, phosphorus and sulphur are removed by using a basic lining.

Open-hearth steel is used for the better class of rails, for railway bridges, for shafts, armor-plate, and heavy guns, and wherever the steel is subject to much vibration.

605. Steel Alloys. We must distinguish between manganese, aluminium, silicon, or titanium added in small amounts ("medicine") to purify the iron, and passing (in combination) into the slag, as described in preceding sections, and the present subject, which concerns *metals added* so as to produce *regular alloys.*

Manganese steel (7 to 20 per cent Mn) is exceedingly hard even when cooled slowly. It therefore does not lose its temper readily when heated by friction. It is used for the jaws of rock crushing machinery and for burglar-proof safes.

Chromium-vanadium steel (1 per cent Cr, 0.15 per cent Va) has great tensile strength, can be bent double while cold, and offers great resistance to changes of stress, and to torsion. It is used for frames and axles of automobiles, and for connecting rods.

Tungsten steel (tungsten 8 to 20%, and chromium 3 to 5%) is used for tools in high-speed metal turning, as it can become red hot (from friction) without loss of temper. Its use has greatly increased the ratio of output to wages.

Nickel steel (containing 2 to 4 per cent of nickel) resists corrosion, and has a very high limit of elasticity and great hardness. It is used for armor-plate, wire cables, and propeller shafts. The alloy with 36 per cent nickel, called **invar,** is practically non-expansive when heated and is valuable for meter-scales and pendulum rods.

5-1-15

606. Properties of Pure Iron. Pure iron may be made by electrolysis, or by reduction of a pure salt by hydrogen. It has a white luster, is very tough, and does not melt below 1510°. The purest iron does *not rust* in cold water.

Ordinary iron *rusts* in moist air or under water, forming a hydrated ferric oxide $3Fe_2O_3,H_2O$. The impurities act as contact agents. The rust is a brittle, porous, non-adherent coating, which does not protect the metal below. Oil protects iron from rusting because, although oxygen penetrates the oil, being soluble in it, moisture does not. Iron displaces hydrogen from hydrochloric and sulphuric acids, giving ferrous salts:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2 \uparrow$$

The impurities — carbide, sulphide, and phosphide — produce hydrocarbons, hydrogen sulphide, and phosphine PH_3, and the last two confer an odor on the escaping gas.

Iron *burns* in oxygen, and *acts* when heated *upon steam*, in both cases producing magnetic oxide of iron Fe_3O_4 (pp. 28, 39). A thin film of this oxide is adherent, and protects the iron ("Russia" iron).

607. Iron has Two Valences. One atomic weight of iron (55.84) may hold two or three atomic weights of a univalent element in combination. Thus, we have ferrous chloride $FeCl_2$ and ferric chloride $FeCl_3$, the bromides $FeBr_2$ and $FeBr_3$, the oxides FeO and Fe_2O_3, ferrous sulphate $FeSO_4$ and ferric sulphate $Fe_2(SO_4)_3$, and so forth. It may therefore be bivalent or trivalent, according to the chemical conditions. For example, in the action of iron on a dilute acid (see equation, above), no ferric salt is formed. Indeed, if ferric chloride is added, the hydrogen and iron reduce it to ferrous chloride (see § 609).

The ferrous salts are *pale green* and give colorless solutions, containing ferrous-ion Fe^{++}. The ferric salts, containing the ion Fe^{+++}, are often *yellow* in solution, on account of ferric hydroxide produced by hydrolysis. The differing properties of the two ions, and the change from ferrous to ferric, and *vice versa,* are discussed below.

608. Ferrous Sulphate $FeSO_4$. When the bath of dilute sulphuric acid, used in cleaning iron for making tin-plate (p. 387), and galvanized iron (p. 334), is becoming exhausted, scrap iron is thrown in to use up the rest of the acid. The solution gives, on evaporation, pale green crystals of **ferrous sulphate,** $FeSO_4,7H_2O$ (**copperas** or **green vitriol**). The salt is used in making ink (see § 616) and rouge (see § 611), and in purifying water (p. 342).

609. Chlorides of Iron. Ferrous Chloride $FeCl_2$ is obtained in solution when iron displaces hydrogen from hydrochloric acid (§ 606), and is isolated by evaporation. The hydrate $FeCl_2,4H_2O$ is pale green, the anhydrous salt colorless. When chlorine is dissolved in the solution, or when the latter, acidified with hydrochloric acid, is exposed to the air, **ferric chloride** $FeCl_3$ is produced:

$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3 \quad \text{or} \quad 2Fe^{++} + Cl_2 \rightarrow 2Fe^{+++} + 2Cl^-$$
$$4FeCl_2 + O_2 + 4HCl \rightarrow 4FeCl_3 + 2H_2O$$

and is familiar in the form of a yellow hydrate $FeCl_3,6H_2O$ obtained by evaporation. Other oxidizing agents, such as nitric acid, produce the same change.

Ferric chloride, in solution, has an *acid reaction*, due to hydrolysis. It is *reduced* to ferrous chloride by shaking the solution, or more quickly by boiling it, with iron filings.

$$2FeCl_3 + Fe \rightarrow 3FeCl_2 \quad \text{or} \quad 2Fe^{+++} + Fe \rightarrow 3Fe^{++}.$$

610. Hydroxides of Iron. Ferric hydroxide $Fe(OH)_3$, appears as a *brown precipitate* when an equivalent amount of sodium hydroxide is added to a solution of a ferric salt:

$$FeCl_3 + 3NaOH \rightarrow Fe(OH)_3 \downarrow + 3NaCl.$$

When only a little sodium hydroxide is added, the brown precipitate, formed locally, redissolves to give a deep reddish solution. This contains ferric hydroxide in *colloidal suspension*. The sodium chloride and unused ferric chloride can be separated by dialysis (p. 305), and a pure colloidal suspension of the hydroxide obtained.

Ferrous hydroxide $Fe(OH)_2$, produced by precipitation, is *white* when pure, but quickly becomes green and then brown by oxidation.

611. Oxides of Iron. When ferric hydroxide is heated, **ferric oxide** Fe_2O_3 remains as a red mass:

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O \uparrow$$

It is made by calcining (roasting) ferrous carbonate, ferrous sulphide, or ferrous sulphate:

$$4FeSO_4 + O_2 \rightarrow 2Fe_2O_3 + 4SO_3.$$
$$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2.$$

The oxide, when pulverized in a ball mill, gives a powder of more or less brilliant red color commonly used in *paints* (**Venetian red** and **Indian red**). That from ferrous sulphate is **rouge,** used in polishing plate glass and lenses, and as a pigment. **Yellow ochre** is a natural hydrated ferric oxide $2Fe_2O_3,3H_2O$, which acquires various depths of color during calcination, and constitutes the **sienna** and **umber** used for paints.

Magnetic Oxide of Iron Fe_3O_4 is regarded as a compound of ferrous and ferric oxides FeO,Fe_2O_3. It is formed by strongly heating ferric oxide:

$$6Fe_2O_3 \rightarrow 4Fe_3O_4 + O_2$$

and is produced when iron is oxidized at a *high temperature* by oxygen, air (blacksmith's scale), or steam. It can be magnetized, and natural specimens are often strongly magnetic (**lodestone**).

Ferrous oxide FeO is a black substance made by cautious reduction of ferric oxide by a stream of hydrogen.

612. Ferrous Carbonate $FeCO_3$. The carbonate occurs in nature as an impurity in clay, in clay iron-stone, and pure as **siderite.** Water containing carbonic acid dissolves it, giving the bicarbonate:

$$FeCO_3 + H_2CO_3 \rightarrow Fe(HCO_3)_2.$$

Thus well and river waters all contain at least traces of ferrous bicarbonate as a part of their hardness. Exposure to the air causes oxidation and, as ferric carbonate is not stable, rust (ferric hydroxide or a hydrated ferric oxide) is deposited:

$$4Fe(HCO_3)_2 + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H_2CO_3.$$

This red deposit is seen in white vessels in which such water drips or stands. It also "yellows" goods washed in such water, if the carbonate of iron is not previously precipitated (p. 326) by soda or some other softening agent (see blueing, § 613).

613. Ferro- and Ferri-cyanides. Potassium ferrocyanide $K_4Fe(CN)_6$, or **yellow prussiate of potash,** is a pale yellow, soluble salt. The iron is contained in the negative radical and ion $Fe(CN)_6^{\equiv\equiv}$, and the solution therefore gives the reactions of this ion, and not of ferrous- or ferric-ion. One of the double decompositions of this salt — namely that with ferric salts — is important because it gives a gelatinous precipitate of **Prussian blue** (ferric ferrocyanide):

$$4FeCl_3 + 3K_4Fe(CN)_6 \rightarrow Fe_4^{III}(Fe(CN)_6)_3^{IV} \downarrow + 12KCl.$$

Prussian blue is employed in making paints, and is the usual pigment in **laundry blueing.** Although insoluble, it is such a fine powder that it appears to dissolve in the water. It is used in the laundry to correct the yellowish tint derived from the ferrous bicarbonate in the water (§§ 534, 612). If the goods are not freed by rinsing from soap and soda, however, the alkali liberated by hydrolysis of the latter enters into double decomposition with the Prussian blue and produces more rust:

$$Fe_4(Fe(CN)_6)_3 + 12NaOH \rightarrow 4Fe(OH)_3 \downarrow + 3Na_4Fe(CN)_6.$$

614. Potassium Ferricyanide $K_3^IFe(CN)_6^{III}$. The difference between this and the preceding salt can be seen by writing the formulæ thus: $4KCN,Fe(CN)_2$ and $3KCN,Fe(CN)_3$. In the ferricyanide the iron is trivalent and the negative ion $Fe(CN)_6^{\equiv}$ is also trivalent as a whole. It is a soluble salt, of brown color, made by oxidizing the ferrocyanide. With ferric salts it gives only a brown solution, but with ferrous salts it gives a deep blue precipitate of ferrous ferricyanide — **Turnbull's blue:**

$$3FeCl_2 + 2K_3Fe(CN)_6 \rightarrow Fe_3(Fe(CN)_6)_2 \downarrow + 6KCl.$$

615. Blue-Prints. Some ferric salts are reduced to ferrous salts when exposed to light. Thus ferric oxalate $Fe_2(C_2O_4)_3$ will keep in the dark, but in light gives ferrous oxalate FeC_2O_4:

$$Fe_2(C_2O_4)_3 \rightarrow 2FeC_2O_4 + 2CO_2 \uparrow$$

When paper is dipped in ferric oxalate solution and dried, and a fern (or ink drawing on transparent paper) is placed over the prepared sheet, sunlight will reduce the iron to the ferrous condition excepting where the fern or ink lines protect it from the light. When the sheet is now dipped in potassium ferricyanide solution (developer), the ferric oxalate gives only the brown substance which can be washed out. But the parts exposed to the light turn deep blue from the precipitation of ferrous ferricyanide in the paper. The pattern is white on a blue ground. In regular blue-print paper ammonium-ferric citrate takes the place of the oxalate, and the ferricyanide has already been applied to the paper, so that only exposure and washing remain to be done.

616. Ink. Writing ink is made by adding to an extract of nut-galls ferrous sulphate, giving ferrous tannate, and acidifying slightly. This salt is soluble and almost colorless, but when spread on paper it is slowly oxidized to the insoluble, black ferric tannate. To make the writing visible from the first, a blue or black dye is added to the ink.

617. Ink, Rust, and Other Stains. Fresh writing **ink,** being soluble, can usually be washed out with water, if the latter is used at once. After the oxidation (§ 616) has occurred, the ferric tannate must be reduced again, by soaking the part for 12 hours or longer in ammonium oxalate solution, and the ink can then be washed out.

Rust stains are often rendered soluble by ammonium oxalate also. Applying hydrochloric acid from a dropping tube, while the cloth is stretched loosely over a cup of hot water, dissolves the rust slowly as ferric chloride. The spot is dipped in the water, between applications of the acid, and finally rinsed with weak ammonia.

Coffee and **tea** stains can be washed out by boiling water, *instantly* applied. Old stains of tea, coffee, or **fruit,** and stains from **dyes,** can be removed only by very dilute hypochlorous acid (mix solutions of bleaching powder and vinegar). Stains on silk can hardly ever be completely removed, and hypochlorous acid must never be applied to them.

Sugar and syrup stains are removed by water. For **grease,** stretch the stained part on blotting paper (to absorb the solution and prevent spreading) and apply the solvent (pp. 85 and 301) in a circle round the spot. For **mixed** stains use the grease solvent first, then, *after it has evaporated,* apply the water or aqueous solution. (For stains produced by indelible ink, see § 666; by paint, see § 635; by **grease,** see pp. 85 and 301.)

618. Other Salts of Iron. Ammonium sulphide solution added to a ferrous salt gives a black precipitate of **ferrous sulphide** FeS. Soluble sulphides blacken the fingers because of the iron, derived from decomposition of proteins, which is present in perspiration.

We can *distinguish ferrous-ion* Fe^{++} from *ferric-ion* Fe^{+++} by the reaction with potassium ferricyanide, which gives a precipitate (blue) with the former only. An equally sharp distinction is obtained by adding potassium sulphocyanate KCNS, for, although the ferrous and **ferric sulphocyanates** are both soluble, the latter is *blood red* in color.

The borax bead, with a particle of an iron compound, gives a green color (**ferrous borate**) in the reducing part of the flame and a yellow color (ferric borate) in the oxidizing part.

COBALT Co AND NICKEL Ni.

619. These metals, like iron, are attracted by a magnet. Cobalt, like iron, has two series of compounds, in which it is bivalent and trivalent, respectively. In its salts, nickel is bivalent only, but the oxide and hydroxide Ni_2O_3 and $Ni(OH)_3$ are also known.

620. Cobalt. Cobaltite CoAsS is one of the chief ores. It is roasted to oxidize the arsenic and sulphur and the oxide of cobalt remains. There are no applications of the metal. Salts are made by the action of acids on the oxide, which is basic.

The metal has a silvery luster, tinged faintly with pink, and does not tarnish. It displaces hydrogen very slowly from dilute *acids*, but is acted upon rapidly by nitric acid.

621. Salts of Cobalt. Cobaltous chloride $CoCl_2,6H_2O$ is red in color, and when partially or wholly dehydrated becomes deep blue. Writing made with a dilute solution of this salt leaves pink traces so faint as to be invisible. But, when the paper is warmed, the hexahydrate is decomposed, and the writing appears blue. When the breath is now blown on the writing, it disappears once more (**sympathetic ink**). **Cobaltous nitrate** $Co(NO_3)_2.6H_2O$ is also a familiar red-colored salt. **Cobaltous sulphide** CoS is precipitated (black) by ammonium sulphide, and is not soluble in dilute hydrochloric acid. Cobalt aluminate $Co_3(AlO_3)_2$ (blue, p. 341) and cobalt zincate $CoZnO_2$ (green, p. 335) afford tests for aluminum and zinc. Borax (bead) gives a deep blue **cobalt borate.**

622. Metallurgy of Nickel. Nickel occurs in all iron meteorites. The chief sources of nickel are **garnierite** (a silicate) from New Caledonia and **pentlandite** (Ni, Cu, Fe)S from Ontario. In the latter case, the ore is roasted and smelted and finally bessemerized (p. 369). The result is an alloy of nickel and copper which is much used for sheet metal work under the name of **monel metal.** Pure nickel is separated from the copper by an electrolytic process (see copper, § 654), or by the Mond process (see nickel carbonyl, § 624). The production of nickel was, in Canada $10,230,000 (1911) and $13,450,000 (1912), and in the U.S. $127,000 (1911).

623. Properties and Uses of the Metal. Nickel is a white, hard, malleable metal which takes, and keeps, a high polish even in moist air. Nickel plating, deposited electrolytically on iron, has the same qualities. The metal is used also in alloys such as **monel metal** (copper, nickel, approximately 1 : 1), **German silver** (copper, zinc, nickel, 2 : 1 : 1), and **nickel coinage** (copper, nickel, 3 : 1). In alloys, although the red color of the copper is completely lost, nickel and copper are simply dissolved and not combined. Zinc and copper, however, give a compound Cu_2Zn_3. **Nickel steel** is used for armor-plate.

624. Compounds of Nickel. These salts are green, and give green solutions (Ni^{++}). The **sulphate** $NiSO_4,7H_2O$ is familiar, as is also the double salt, **ammonium-nickel sulphate** $(NH_4)_2SO_4,NiSO_4.6H_2O$, used in nickel plating. The **sulphide** NiS (black) behaves like cobalt sulphide. **Nickel carbonyl** $Ni(CO)_4$ is a volatile, colorless liquid (b.-p. 43°). It is formed by passing carbon monoxide over warm, finely divided nickel, and is decomposed again, yielding nickel 99.6 per cent pure, by heating at 180°. These actions are the basis of the Mond process for separating nickel from the alloy obtained from pentlandite (§ 622). The borax bead is reddish-brown (**nickel borate**) when oxidized, and colorless, but turbid (metallic nickel), when reduced.

625. Exercises.

1. Why does paint protect iron from rusting?

2. Why does iron, in time, turn completely into rust, while zinc and aluminium receive only a slight film of tarnish?

3. How could it be ascertained that ferric hydroxide is in colloidal suspension, and not dissolved?

4 Make equations for: (a) the interaction of potassium ferrocyanide and cupric sulphate $CuSO_4$, giving a brown precipitate of cupric ferrocyanide; (b) the action of hydrochloric acid on ferric hydroxide (or rust).

5. In removing a mixed stain, why allow carbon tetrachloride (*e.g.*) to evaporate, before applying water (to remove sugar, *e.g.*)?

CHAPTER XXXVIII.

LEAD AND TIN.

626. Lead and tin are the best-known metallic members of the family, to which the non-metals silicon and carbon also belong. In their compounds they are bivalent or quadrivalent.

LEAD Pb.

627. Metallurgy of Lead. The chief ore of lead is **galenite** PbS. The ore, if rich, is roasted in a reverberatory furnace (Fig. 92, p. 367) until a part has been converted into the oxide PbO and sulphate $PbSO_4$. The air is then shut off, and the temperature raised, so that these products may oxidize the remaining galenite:

$$PbS + 2PbO \rightarrow 3Pb + SO_2 \uparrow$$
$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2 \uparrow$$

The melted lead flows out.

When the ore is poor, it is treated at a red heat for 24 hours with lime and air, giving a mixture of PbS with $PbSO_4$ and calcium sulphate. Further roasting converts all the lead to PbO, which is then reduced with coke in a closed furnace.

The lead contains silver and some gold, which are recovered by Parke's process (see silver, § 663).

628. Properties of Lead. Lead is a soft *malleable* metal, with a bluish-white or grey *luster* when freshly cut. It is quickly, but only superficially, oxidized by the *air*. It acts slowly upon hydrochloric acid, but not upon cold sulphuric acid. With nitric acid it gives lead nitrate $Pb(NO_3)_2$ and oxides of nitrogen. Soft water, in presence of air, dissolves it in appreciable amounts as hydroxide $Pb(OH)_2$, and carbonic acid assists the process. Hard water, however, produces a skin of carbonate and sulphate (insoluble) which protects the surface. Hence lead pipes may be used for hard water, but not for rain water. In presence of air, acids (even feeble vegetable acids) interact with the metal, which is therefore unsuitable for kitchen utensils.

The compounds of lead are *poisonous* and, not being eliminated, accumulate in the system. For this reason the manufacture and use of white lead are forbidden in France (laws of 1906 and 1912), and are subject to detailed regulation in Germany.

629. Uses of Lead. The metal is rolled into sheets, which are used for lining tanks. Lead pipes are made by pressing the metal, while hot, through dies. Their pliability, and the ease with which they can be cut and soldered, fits them for use in plumbing and for covering electric cables.

Type metal, containing 20 per cent of antimony, is harder than lead, and expands on solidifying. Small **shot** (p. 267) contain 0.5 per cent of arsenic. **Solder** (lead, tin 1 : 1) remains melted at a lower temperature than pure lead (m.-p. 326°) and so can be applied to a lead joint without danger of melting the lead itself. Pure melted lead would almost always be above 326°, and would melt the leaden object to be soldered (see § 640, Ex. 2).

630. Oxides. Lead monoxide PbO is made by oxidizing melted lead in a current of air. At low temperatures a buff colored powder, **massicot,** is obtained. When the oxide is allowed to melt, it solidifies to a reddish-yellow, scaley mass — **litharge.** The oxide is predominantly basic, absorbing carbon dioxide from the air and, with acids, giving salts. It is used in making glass and enamels. Stone and glass can be cemented with a mixture of massicot and glycerine.

Minium or **red lead** Pb_3O_4 is a bright-red powder formed by oxidizing the monoxide in air at 470 to 480°.

$$6PbO + O_2 \rightleftarrows 2Pb_3O_4.$$

Red lead is used in making flint glass and as the basis of the red paint (see § 634) applied to iron. Moistened with linseed oil (§ 634), it is used by plumbers to make joints tight.

Lead dioxide PbO_2 is a brown powder, made by treating red lead with diluted nitric acid.

631. Lead Acetate. Lead monoxide dissolves in boiling vinegar or acetic acid to give the **acetate (sugar of lead)** a white soluble substance:

$$PbO + 2HCO_2CH_3 \rightarrow Pb(CO_2CH_3)_2 + H_2O.$$

Additional lead oxide can be dissolved in the neutral solution to give a basic acetate, $2Pb(CO_2CH_3)_2,Pb(OH)_2$.

632. White Lead. The ordinary carbonate $PbCO_3$ has no applications. White lead is a **basic carbonate** $2PbCO_3, Pb(OH)_2$. It is a heavy, white, insoluble, amorphous substance. Mixed with linseed oil, it forms a white paint valued for its "body" or covering power (opacity). Other pigments are added to give the required color. Its disadvantage is the darkening, due to formation of the black lead sulphide PbS, which is produced by the hydrogen sulphide in the air.

The old **Dutch process** is still used extensively. Gratings ("buckles") of lead are placed above a little vinegar in small pots. The pots are covered with boards, on which manure or spent tan bark is spread. Other tiers of pots, boards, and bark are placed on the first, until the shed is full. Carbon dioxide, warmth, and moisture are furnished by the decaying bark. The gratings, by the end of three months, are converted into cakes of white lead:

$$\begin{array}{l}
2Pb + 2CO_2 + O_2 \rightarrow 2PbCO_3 \quad \times 2 \\
2Pb + 2H_2O + O_2 \rightarrow 2Pb(OH)_2 \\
\hline
6Pb + 4CO_2 + 2H_2O + 3O_2 \rightarrow 2(2PbCO_3,Pb(OH)_2)
\end{array}$$

The vinegar may be regarded as a catalytic agent. It produces the basic acetate (§ 631), which is decomposed by the carbonic acid with liberation of the acetic acid once more. The white lead is ground, first under water, and then in oil.

In **Mild's process** (used *e.g.* by the Acme Co., Detroit) melted lead is atomized by a jet of steam, and the lead dust is beaten in a vat for about seven days with vinegar, air, and carbon dioxide. In the **French process** white lead is precipitated by a stream of carbon dioxide from a *solution* of the basic acetate.

633. Other Compounds of Lead. Lead chromate $PbCrO_4$ is precipitated by adding potassium chromate (or dichromate) solution to a solution of a salt of lead. It is used as a pigment (**chrome-yellow**). **Lead chloride** $PbCl_2$ (white) is slightly soluble in cold water and the **iodide** PbI_2 (yellow) is insoluble. Both are formed by precipitation. **Lead sulphide** PbS (black) is precipitated by hydrogen sulphide, even from acid solutions (see picture restoring, p. 231). The **sulphate** $PbSO_4$ is the most insoluble salt. On this account, the workmen in white lead works add a little sulphuric acid to the water they drink.

Zinc, or any of the metals more active than lead, when placed in a solution of a soluble salt of lead, will displace the metal, and deposit it in a mossy form ("lead-tree"):

$$Zn + Pb^{++} \rightarrow Zn^{++} + Pb \downarrow$$

634. Paints. A paint consists of a suspended solid powder, and a "drying" oil which will harden to a tough resin on exposure to the air and attach itself securely to the surface. The solid powder (pigment) gives opacity and, when desired, color to the paint. Since it does not shrink, it also "fills" the paint, and prevents the formation of minute pores which otherwise would be found in the "dried" oil. The pigment is thus necessary to enable the paint to protect the object from the action of the oxygen and moisture in the air.

The "dryer" does not dry by evaporation, but gives a resin by oxidation. Linseed oil and hemp oil are examples. They contain glyceryl esters of *unsaturated* acids, such as that of linoleic acid $C_3H_5(CO_2C_{17}H_{31})_3$ which contains four units of hydrogen less than stearic acid (p. 298). Boiling before use makes the esters more rapidly oxidizable by air. The cement of red lead and oil (§ 630) sets rapidly because the red lead itself oxidizes the oil.

635. Removal of Paint Spots. Paint spots are removed by backing the material with blotting paper and applying turpentine (not to silk) or benzine to dissolve the resin. The loosened pigment can then be brushed out. Varnish can usually be removed with alcohol. Pitch (hydrocarbons) is removed by kerosene, because all hydrocarbons are mutually soluble.

TIN Sn.

636. Metallurgy. Tin is obtained from **cassiterite** or tinstone SnO_2 (stannic oxide). The largest supply comes from the East Indies, the next largest from Bolivia, and the third largest from Cornwall. The ore is roasted to expel sulphur and arsenic, and reduced with coal in the reverberatory furnace. The melted metal is cast in blocks ("block tin"). The metal was well known to the ancients (found in Egyptian tombs).

637. Properties. The metal is *white*, and markedly crystalline. It is *soft* and *malleable* (tinfoil), and *melts* at 232°.

Tin does not tarnish in the *air*. With concentrated *acids* it acts rapidly. Hydrochloric acid gives stannous chloride $SnCl_2$ and hydrogen. Concentrated sulphuric acid gives stannous sulphate $SnSO_4$, sulphur dioxide (§ 352), and water:

$$Sn + 2H_2SO_4 \rightarrow SnSO_4 + SO_2 \uparrow + 2H_2O.$$

Nitric acid gives the insoluble, white meta-stannic acid H_2SnO_3:

$$4HNO_3 + Sn \rightarrow H_2SnO_3 \downarrow + 4NO_2 + H_2O.$$

638. Uses. Tin plate, used in making "tin" cans, is produced by dipping cleaned sheets of mild steel in melted tin. So long as the layer of tin remains intact, the iron is protected from rusting. But, if the tin layer is damaged, the iron rusts. The iron being the more active metal of the two, the tin acts as a contact agent and actually hastens the rusting.

Scrap tin plate from can factories, bearing 3 to 5 per cent of tin, is "detinned." In the Goldschmidt process the scrap is cleaned, dried, and exposed to dry chlorine, which converts the tin into the liquid stannic chloride $SnCl_4$, but leaves the iron unaffected (p. 110). The chloride is used in mordanting.

Copper vessels for cooking and brass pins are also coated with tin, to preserve them from the action of air and moisture. Tin pipes are used where lead would be unsafe, as, for example, for soda-water and beer.

Tin enters into many useful alloys, such as bronze (with copper) and solder.

639. Compounds of Tin. **Stannous chloride** $SnCl_2,2H_2O$, "tin crystals," and a hydrate of **stannic chloride** $SnCl_4,5H_2O$ are used in mordanting. With soda the former gives **stannous hydroxide** $Sn(OH)_2$ and the latter **stannic acid** $Sn(OH)_4$, both gelatinous substances which are precipitated in the goods to be dyed. Stannic acid is also sometimes precipitated in flannelette (a material made of cotton) to render it non-imflammable, and always in silk to "weight" it (the increase may be from 25 per cent to 300 per cent or more).

Stannous sulphide SnS (brown) and **stannic sulphide** SnS_2 (yellow) are precipitated by hydrogen sulphide, even from acid solutions of stannous and stannic salts, respectively. They both interact with a solution of ammonium polysulphide and dissolve.

640. Exercises.

1. Make equations for: (a) the action of air and water on lead to form the hydroxide; (b) the formation of basic lead acetate by dissolving lead oxide in lead acetate solution; (c) the action of hydrogen sulphide on white lead; (d) the precipitation of $PbCl_2$ and of PbI_2.

2. Tin melts at 232° and lead at 326°. Solder (1 : 1) melts (and solidifies) at 210°. Why is this? What is the advantage of using solder?

3. Make equations for: (a) the action of soda on solutions of stannous and stannic chlorides, respectively; (b) the action of hydrogen sulphide on the same salts.

CHAPTER XXXIX.

COPPER AND MERCURY.

641. In this chapter we encounter the first metals (if we except As and Sb) which are *below* hydrogen in the activity list, and do not displace that element from dilute acids. Copper and mercury both have *two valences*, so that we have cupric-ion Cu^{++} and cuprous-ion Cu^{+} and mercuric-ion Hg^{++} and mercurous-ion Hg^{+}. All the soluble compounds of both are *poisonous.*

COPPER Cu.

642. Occurrence. Copper occurs *free* in considerable amounts, particularly on the Michigan shore of Lake Superior. **Cuprous oxide** Cu_2O and basic carbonates, like **malachite** $CuCO_3,Cu(OH)_2$, are less common. The latter is often used as an ornamental stone. A large proportion of commercial copper is obtained from **chalcopyrite** Cu_2S,Fe_2S_3.

643. Metallurgy. The free copper, after being concentrated (freed from gangue) by washing, is smelted with a flux. The carbonate is roasted, leaving the oxide. The oxides are reduced with coal.

The sulphide ores are more difficult to reduce, and the presence of so much iron complicates the process. They are *first* roasted. This removes much of the sulphur as sulphur dioxide, leaving Cu_2O and Fe_2O_3. Next the roasted material is treated in a blast furnace, along with " green " (unroasted) ore, sand (if silica is not present in the ore), and coke. Some of the iron is oxidized and removed in the slag (as silicate). The product, known as copper " matte," is a mixture of cuprous sulphide Cu_2S with ferrous sulphide FeS. The *third* stage is to bessemerize the melted matte with sand in a converter. Here the rest of the iron is oxidized and eliminated as silicate in the slag, and the sulphur escapes as SO_2. The slag and metallic copper are poured separately. The latter gives off some dissolved sulphur dioxide in bubbles as it solidifies and, from its appearance, is named **blister copper.** *Finally*, since the copper now contains dissolved cuprous oxide Cu_2O, the blister copper is melted and "poled," by stirring with green wood. The gases (hydrocarbons, etc., § 573) given off by the heated wood reduce the oxide to copper. If the copper is to be refined electrolytically (§ 654), it is then cast in plates 3 feet square and ¾ inch thick.

644. Properties. Copper has a characteristic, bright, yellow-pink *luster*, quickly darkened by oxidation. It is second only to silver in *electrical conductivity* and to iron in *tenacity*. It is third in order of *malleability* (Dutch-leaf is used in gilding). It *melts* at 1057°.

In moist *air* copper acquires a green coating of basic carbonate, which protects the metal. It is little affected by dilute hydrochloric or sulphuric *acids*, when air is excluded. Hot concentrated sulphuric acid gives cupric sulphate and sulphur dioxide (p. 219), and nitric acid gives cupric nitrate and oxides of nitrogen (p. 244).

645. Uses. Pure copper is used for electric wires and cables. Traces of other metals greatly reduce the conductivity. Kettles, stills, and evaporating pans are made of copper. It is used for sheathing ships and for bolts, because it resists corrosion by sea water.

It enters into important *alloys*, such as **brass** (18 to 40 per cent of zinc), and **bronze** for coins (4 per cent tin and 1 per cent zinc), for gunmetal (10 per cent tin), and for bell-metal

(20 to 24 per cent tin). Aluminium bronze (5 to 10 per cent aluminium) is used for the hulls of yachts. All of these are composed in part of compounds, such as Cu_3Sn and Cu_2Zn_3.

646. Cupric Sulphate $CuSO_4,5H_2O$. The hydrated sulphate, **bluestone** or **blue vitriol**, is made by continuously agitating granulated copper with air and warm dilute sulphuric acid:

$$2Cu + O_2 + 2H_2SO_4 \rightarrow 2CuSO_4 + 2H_2O.$$

The *blue* crystals form on strips of lead suspended in the warm, saturated solution.

Because of slight hydrolysis, giving an active acid and a weak base $Cu(OH)_2$, the aqueous solution is *acid* in reaction.

Cupric sulphate is used in battery solutions. The salt is employed in minute proportions to destroy algæ, which otherwise confer a disagreeable taste and odor on water that has been standing in reservoirs. Seed for cereals is moistened with a dilute solution to prevent "smuts." It is used in making Bordeaux mixture (§ 647).

647. Cupric Hydroxide $Cu(OH)_2$. The hydroxide is a *blue*, gelatinous *precipitate*, formed when an alkali is added to cupric sulphate solution. It is used as a mordant. A mixture of cupric sulphate solution and milk of lime ($Ca(OH)_2$), — **Bordeaux mixture** — containing this precipitate, is used extensively as a spray on grape vines and other plants, to prevent the growth of fungi.

Cupric hydroxide *dissolves* in ammonium hydroxide solution, giving a liquid of deep blue color (containing $Cu(NH_3)_4(OH)_2$) which is employed (p. 314) as a solvent for cellulose. It *dissolves* also in a solution of Rochelle salt (p. 280), giving **Fehling's solution**, a reagent used in testing for glucose and similar reducing agents. When this reagent is added to a liquid containing glucose (p. 181), red, hydrated cuprous oxide Cu_2O is precipitated.

648. Cuprous Oxide Cu_2O. This oxide, mixed with CuO, is formed by gentle heating of copper in air, and is best prepared by use of Fehling's solution (§ 647). It is employed in making ruby glass and in coloring porcelain.

649. Cupric Oxide CuO. When the liquid containing the blue precipitate of cupric hydroxide (§ 647) is boiled, the blue color changes to *black* and cupric oxide is thrown down:

$$Cu(OH)_2 \rightarrow CuO + H_2O.$$

The same oxide is made by heating cupric nitrate (p. 245) or carbonate.

650. Organic Analysis. The oxide is used in the laboratory to ascertain the compositions (and formulæ) of organic compounds (**determination of carbon and hydrogen**). A weighed amount of the organic compound is placed in a horizontal tube, between heated masses of the oxide. A stream of oxygen or air carries the vapor of the organic compound over the cupric oxide, which oxidizes it to water and carbon dioxide. The first is absorbed in a weighed U-tube filled with calcium chloride, and the second is caught in a weighed vessel containing potassium hydroxide. From the increase in weight in each case, the corresponding weights of hydrogen and carbon (derived from the weighed portion of the organic compound) are calculated.

651. Other Compounds of Copper. Hydrogen sulphide precipitates **cupric sulphide** CuS (brownish-black) even from acid solutions of cupric salts. When a particle of a compound of copper is fused with borax (bead), *blue* **cupric borate** is formed.

More active metals, such as zinc or iron, displace copper from solutions of its salts, so that a blade of a knife, for example, receives instantly a red coating of copper when immersed in such a solution:

$$Fe + Cu^{++} \rightarrow Fe^{++} + Cu \downarrow$$

652. Copper Plating. When platinum or carbon plates, connected with a battery, are immersed in a solution of cupric sulphate, copper is deposited on the negative plate (cathode). The $SO_4^{=}$ migrates (p. 133) towards the positive wire (anode) and there produces oxygen and sulphuric acid:

$$2SO_4 + 2H_2O \rightarrow 2H_2SO_4 + O_2 \uparrow$$

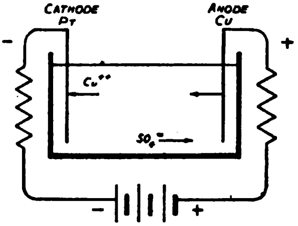


Fig. 95

If the anode is made of copper itself, however, the $SO_4^{=}$ migrates, but is not discharged. Instead, copper goes into solution (Fig. 95) as Cu^{++}, in amount equal to that deposited on the other plate. Thus the quantity of cupric sulphate in solution remains unchanged, and the effect is, virtually, to transfer copper from the copper anode to the cathode.

653. Electrotypes. A copper *electrotype* of an object like a medal is made by first preparing a cast of the medal in plaster of Paris or wax. The surface of this is rubbed with graphite, to render it a conductor, and the cast is used as the cathode in a cell like that just described. The deposit of copper, when stripped off, is found to show an exact reproduction of the engraving, etc., on the object.

Book plates are made by taking a cast of each page of type, preparing the copper electrotype, and then strengthening and thickening it by filling the back with melted lead. The printing is then done from the electrotype. For newspapers this process is too slow, and the plate is made from the cast by means of melted stereotype-metal (lead, antimony, tin; 82 : 15 : 3).

654. Copper Refining. The copper, as obtained from the ores by the treatment already described (§ 643), contains a certain amount of silver, gold, and baser metals. The former pay for the cost of refining, and the simultaneous removal of the latter gives pure copper suitable for electrical purposes.

The principle is the same as that used in electroplating. The heavy plates of poled copper (§ 643) are hung at intervals in large, lead-lined vats of copper sulphate solution and form the anodes (Fig. 96, diagrammatic, view from above). The metal is deposited on thin sheets of copper, which are coated with graphite to permit the deposit to be easily stripped off. These sheets hang in the vat between the anodes, and are connected with the negative wire. The copper, along with such traces of more active metals, like zinc (see activity list), as are present, is ionized and goes into solution, until the anode is reduced to a skeleton and is exchanged for a fresh one. The less active metals, such as silver and gold, as well as traces of sulphides, are not ionized. They fall to the bottom of the vat, as a sort of heavy mud. At the cathode copper ions alone are discharged, and deposited, because copper is the least active of the metals present in ionic form. In this way copper, 99.8 per cent pure, can be obtained, and gold and silver are recovered from the mud.

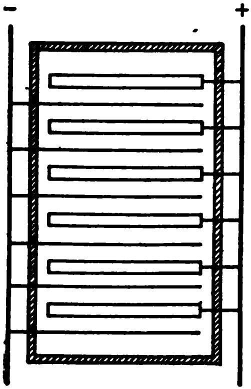


Fig. 96

655. Nickel Plating. Here the bath contains an ammoniacal solution of ammonium-nickel sulphate (p. 380), and a plate of nickel forms the anode. The article to be plated is carefully cleaned, to secure a uniform deposit, and is suspended as cathode in the vat. The surface of the deposit is afterwards burnished.

MERCURY Hg.

656. Metallurgy. Mercury occurs both free and as mercuric sulphide HgS, **cinnabar,** and usually in the same localities. Most of the ore comes from California and Spain (Tarshish). Decoration with "rubies of Tarshish" refers to tattooing with powdered cinnabar (red).

The ore is roasted, sulphur dioxide escapes, and the vapor of mercury is condensed in long, tortuous flues.

657. Properties. Mercury is a *liquid* at ordinary temperatures, hence its name, **quicksilver** (*i.e.* live silver). It *freezes* at −40°, and *boils,* giving an invisible, vapor, at 357°. The vapor density shows the molecules to be *monatomic,* as indeed are the molecules of all metals of which the vapor densities have been measured.

The metal has a silvery metallic *luster*, which is not affected by the air, and a high specific gravity (13.6).

Mercury dissolves other metals, forming *alloys* or **amalgams.**

Mercury vapor, and mercury when finely divided, are poisonous. Small amounts are triturated with honey and mixed with pulverized roots in making **blue pills,** and with greasy substances in making mercurial ointments.

Mercury, when moderately heated, combines with *oxygen,* forming mercuric oxide (red), but the action is reversible, and the oxide is decomposed by stronger heating (p. 20). It combines readily with sulphur and the halogens. Dilute hydrochloric and sulphuric *acids* are not attacked by mercury. Concentrated nitric acid attacks and dissolves it as nitrate readily.

658. Uses. Mercury is used in filling thermometers and barometers. Sodium **amalgam** is used in the laboratory and the zinc plates of batteries are amalgamated superficially to protect them when the battery is not in use. Dentists fill teeth with mixtures of mercury with silver, copper, cadmium and other metals, which quickly set to a solid amalgam. The pulverized ores of gold and silver, mixed with water, are allowed to trickle over thin layers of mercury. The latter dissolves the particles of the precious metals, while the sand passes on (see § 669).

659. Compounds of Mercury. As in the case of copper, there are two sets of compounds — mercurous Hg^{I} and mercuric Hg^{II}. All the common salts are completely *volatile,* with or without decomposition, when strongly heated (vapor poisonous!).

Mercuric chloride or **corrosive sublimate** $HgCl_2$ is made by subliming a mixture of mercuric sulphate and sodium chloride. It is a white substance, soluble in water. Hydrogen sulphide precipitates **mercuric sulphide** HgS (black) from the solution. Mercuric chloride is a violent poison. A very dilute solution is used as an antiseptic. Great precautions should be taken, however, to make impossible the accidental swallowing of the antiseptic tabloids, as each contains enough of the material for several fatal doses. Albumen (white of eggs) forms insoluble compounds with it, and is used as an antidote.

Mercurous chloride or **calomel** $HgCl$ is precipitated as an amorphous white powder when a chloride is added to a solution of a mercurous salt. It is used in medicine to stimulate all organs producing secretions. Ammonium hydroxide changes calomel to a black mixture of free mercury and mercuric amidochloride $Hg(NH_2)Cl$. **Mercuric fulminate** $Hg(ONC)_2$ is used in percussion caps (p. 311).

Baser metals precipitate mercury from solutions of its salts. The grey deposit is best seen on a clean strip of copper foil:

$$Cu + Hg^{++} \rightarrow Cu^{++} + Hg \downarrow$$

660. Exercises.

1. Make an equation: (a) for the oxidation of ethyl alcohol by heated cupric oxide; (b) for the precipitation of cupric sulphide from cupric sulphate solution.
2. When we electrolyzed sodium chloride solution (p. 106), hydrogen was liberated at the cathode. What principle, used in the electrolytic refining of copper, does this phenomenon illustrate?
3. How could you recognize cupric sulphate solution by showing that it contained, (a) cupric-ion, (b) sulphate-ion (p. 224)?
4. Make an equation for the liberation of mercury from cinnabar.
5. What gases should you collect over mercury?
6. What other salts, beside those of mercury, are volatile?
7. How should you recognize a salt of mercury in solution?

Items 40 + 41

Also 8 questions on Ch 38 – 41

CHAPTER XL.

SILVER, GOLD, PLATINUM.

661. Descending the activity list, we now reach the "noble" metals, which are the least active. They do not combine with oxygen, even when heated. Silver and gold have long been in use.

SILVER Ag.

662. Occurrence. Native silver is found in many localities, usually in small amounts. The chief supply of the metal is obtained from the ores of lead and copper, which contain silver sulphide Ag_2S. The chief localities are in California, Australia, and Mexico.

663. Metallurgy. After the lead (bearing silver) has been extracted from the ore (p. 382), it is melted in large caldrons, a small proportion of zinc is added, and the whole is vigorously stirred (**Parke's process**). Zinc is only slightly soluble in lead, but it combines with silver in several proportions. The zinc-silver alloy rises to the surface, solidifies (while the lead is still molten), partly as alloy and partly as a compound (usually Ag_2Zn_5), and is skimmed off. The most of the adhering lead is pressed out, and the compound (or mixture) is placed in graphite retorts, in which the zinc is removed by distillation. The silver and lead which remain are heated in a blast of air (**cupelled**) to oxidize the lead. The melted litharge flows off and the silver is then cast.

The gold, which accompanies the silver through this treatment, is separated electrolytically (see copper, § 654). The silver-gold alloy forms the anode, and silver nitrate the vat-liquid. The silver, being the more active metal, is ionized and deposited on the cathode, while the gold collects as a powder in a bag which surrounds the anode.

An older method, still used, is to heat the silver with concentrated sulphuric or nitric acid, either of which will dissolve the silver and leave the gold. From the solution the silver is displaced by the action of plates of copper:

$$Cu + 2Ag^+ \rightarrow Cu^{++} + 2Ag \downarrow$$

Over sixty million ounces (troy) of silver are obtained annually in the United States (1911), this being about one-third of the world's production.

664. Properties. Silver is fairly *hard*, considering its great *ductility* and *malleability*. It is the best *conductor* of electricity.

When an electric discharge passes between the ends of two silver wires, held under water, silver is dispersed at the points and forms a *colloidal solution*. The color of the solution varies from brownish to pink, according to the conditions. Colloidal solutions of gold and platinum can be made in the same way.

The metal is oxidized by ozone (p. 229), although not by oxygen. Sulphur compounds in the air *tarnish* the surface (Ag_2S, for details, see § 344), as do also eggs, secretions from the skin (see proteins, p. 348), and vulcanized rubber (§ 171).

Cold nitric *acid* and hot concentrated sulphuric acid are attacked by it, giving the nitrate and oxides of nitrogen, and the sulphate and sulphur dioxide, respectively:

$$3Ag + 4HNO_3 \text{ (dil.)} \rightarrow 3AgNO_3 + 2H_2O + NO \uparrow$$

665. Uses. For silver ware and coins the metal is alloyed with copper. American and Continental coins contain 90 per cent of silver ("900 fine"). British coins are 925 fine, which is the proportion in "sterling silver." Articles of baser metal are *plated* with silver. The bath contains **potassium argenticyanide** $KAg(CN)_2$, made by adding potassium cyanide in excess to silver nitrate solution:

$$KNC + AgNO_3 \rightarrow KNO_3 + AgCN.$$

This solution gives a compact deposit. The anode is of silver, so that the silver in the solution is replenished as quickly as it is deposited.

Mirrors are silvered by cleaning the surface and pouring over it a solution containing silver nitrate, ammonium hydroxide, and a reducing agent like formaldehyde CH_2O, or grape sugar:

$$4AgOH + CH_2O \rightarrow 3H_2O + 4Ag \downarrow + CO_2.$$

The film of silver adheres to the glass and is washed, dried, and varnished.

666. Silver Nitrate $AgNO_3$. This salt is deposited from solution (§ 664) in colorless crystals. Its solution is *neutral* in reaction, which shows that silver hydroxide is not a weak base. It melts easily and is cast in sticks (**lunar caustic**), which are used in cauterizing sores. It is the chief source of the other compounds of silver. It is used in some hair dyes, and in **indelible ink.** In the latter case the organic matter in the goods reduces it, with the help of light, to metallic silver. Sodium thiosulphate solution (see §§ 667, 668) will very slowly *remove* the stain.

667. Silver Halides. Silver chloride AgCl is precipitated (white) when a soluble chloride is added to a solution of a salt of silver:

$$AgNO_3 + KCl \rightarrow AgCl \downarrow + KNO_3.$$

Silver bromide AgBr is precipitated with bromide-ion and **silver iodide** AgI with iodide-ion. These compounds have a yellowish tinge. The chloride and bromide are easily dissolved by ammonium hydroxide solution, giving the ion $Ag(NH_3)_2^+$, and also by sodium thiosulphate solution $Na_2S_2O_3$ ("hypo").

All the halides of silver are decomposed by light, which liberates the halogen, and finally leaves metallic silver.

668. Photography. The taking of a photograph involves four processes — preparation of the plate, exposure, development, and fixing.

Silver bromide is precipitated in an aqueous suspension of gelatine. The mixture is kept warm, to permit the precipitate to become more sensitive to light by acquiring a coarser grain ("ripen"). The "emulsion" is applied to plates of glass or strips of transparent celluloid (films).

The brief **exposure** to the image of the object, well-focussed in the camera, produces no visible effect. But the bromide is thereafter more easily reduced to metallic silver, in proportion to the intensity of the light that fell upon each part.

Development consists in applying a reducing agent, of such slight activity that its effect during the process on non-illuminated parts of the bromide is practically zero. Ferrous oxalate, or an alkaline solution of pyrogallic acid or of hydroquinone, may be used. The reduction goes fastest and deposits most silver when the illumination was most intense. Thus, the plate becomes most opaque where the object was brightest, and *vice versa*. On account of this reversal, the plate is called a *negative*. With the potassium salt of hydroquinone $C_6H_4(OH)_2$, quinone $C_6H_4O_2$ is formed:

$$2AgBr + C_6H_4(OK)_2 \rightarrow 2Ag + 2KBr + C_6H_4O_2.$$

The foregoing processes are all carried out in a faint red light, which is almost without action on silver bromide. To prevent the gradual reduction of the remaining, unchanged bromide to silver by daylight, it is dissolved out by soaking the plate in "hypo" (**fixing**). The plate is now *clear* where no silver was deposited. The negative is finally washed thoroughly to remove all except the gelatine and the silver image, and is then dried.

In **printing** the prepared paper is illuminated *through* the negative, and light and dark are again reversed. The denser parts of the negative protect the paper below them, and leave these parts white. On *printing out paper*, silver chloride suspended in egg albumen is the sensitive substance, and the silver is liberated in a reddish, colloidal condition. The color is improved by *toning* with a solution containing gold chloride, as part of the silver goes into solution and gold (purplish) is deposited in its place. The print is fixed with hypo, washed, and dried. *Developing papers* like velox (invented by Baekeland) are essentially like plates (silver bromide in gelatine), and are exposed, developed, and fixed in the same way.

The making of blue prints has already been described (p. 377).

GOLD Au.

669. Occurrence and Extraction. Gold is found in the *free* condition in veins of quartz in almost every part of the world. Alluvial deposits, resulting from the breaking up of such rock, contain gold also, and nuggets weighing many pounds have been discovered. It is found also in combination with tellurium, an element resembling sulphur.

In **vein mining** (*e.g.* in the Transvaal) the rock is pulverized with iron stamps working in an iron trough. The powder is washed in the form of mud over plates of copper amalgamated with mercury, in which 55 per cent of the gold dissolves. The amalgam is afterwards scraped off, the mercury removed by distillation, and the gold residue refined. The tailings still contain 45 per cent of the gold, adhering to the particles of rock. They are covered with sodium cyanide (p. 328) solution, and exposed to the air, until the gold has been dissolved as sodium aurocyanide $NaAu(CN)_2$. From this solution the gold is deposited by electrolysis, or displaced by zinc.

The alluvial deposits are washed, on a small scale, in "cradles" (shallow pans) and, on a large scale, by being carried by water down a long trough (**Placer Mining**). The gold, having a much higher specific gravity than the rock, sinks to the bottom, while the rock particles are carried away. In the trough the gold settles between cleets nailed across the bottom. In **hydraulic mining**, a modification of placer mining, very heavy streams of water are thrown against the deposit.

Over one-fourth of the world's supply comes from the United States (4,700,000 ounces in 1911) and a little less than one-fourth each from South Africa and Australia.

670. Properties. Gold is yellow in *color*, copper being the only other familiar metal which is colored. It is the most *malleable* and *ductile* of metals. It *melts* at 1075°. To enable it to resist wear, it is alloyed with copper. Pure gold is "24 carat" fine. British gold coins are 22 carat, and American, French and German coins 21.6 carat (90 per cent gold).

Gold is not affected by *oxygen* or by hydrogen sulphide. It does not interact with any single *acid*. It combines directly, however, with chlorine and bromine. It dissolves in *aqua regia* (hydrochloric and nitric acids, mixed). This happens, not because *aqua regia* is more active as an oxidizing agent than the substances it contains, but because it oxidizes, and *also* furnishes the chloride-ion Cl^- required to produce the *exceedingly stable negative ion* of chlorauric acid $HAuCl_4$, namely $AuCl_4^-$.

671. Uses. Most of the metal is used in coins and bars as a medium of exchange. It is beaten into gold leaf. It is employed in making **potassium chloraurate** $KAuCl_4$ for toning. Gold plating on silver and other metals is carried out by using a gold anode and a bath of **sodium aurocyanide** $NaAu(CN)_2$ solution.

PLATINUM Pt.

672. Occurrence and Extraction. Platinum is found in the free condition in alluvial sand, and chiefly in the streams of the Ural Mountains and the Caucasus. The separation from osmium, iridium, and other metals, which accompany it, is a complex operation.

673. Properties. Platinum is a *malleable* and *ductile* metal with a greyish-white *luster*. It *melts* in the oxy-hydrogen flame (m.-p. about 1780°), but not in the Bunsen flame.

The metal is not affected by *air*, *water*, or *acids*, excepting *aqua regia*. In the latter instance, **chloroplatinic acid** H_2PtCl_6 is formed.

Platinum *absorbs* hydrogen and oxygen. When finely divided, so as to present a large surface, it *catalyzes* powerfully many chemical actions. Amongst the forms used are **platinum black,** a powder precipitated from chloroplatinic acid by an active metal (*e.g.* zinc); **platinum sponge,** a porous mass made by decomposing ammonium chloroplatinate by heat; and **platinized asbestos** (p. 223), made by dipping the asbestos in chloroplatinic acid solution and heating.

It *unites*, slowly, with chlorine and bromine. It combines also with carbon, phosphorus, and silicon, and alloys itself with many metals, so that reactions which liberate any of these elements can not be carried out in vessels of platinum. It also acts upon fused caustic alkalies giving platinates.

674. Uses. Since the metal does not melt in the Bunsen flame, and is not affected by many substances, it is employed in laboratory operations in the forms of wire, foil, and crucibles. Much of the metal is used by dentists, and in photography. Having the same expansibility as glass, it was for many years fused through the bottom of every incandescent lamp, to connect the filament with the exterior. A substitute has now taken the place of platinum in such lamps. Since the metal is not oxidized by the air, even when heated, it is used for electrical contacts. The metal is employed also for jewelry and, in Russia, for coinage. An alloy with iridium, offering special resistance to both chemical and mechanical wear, is used for the international standards of length and weight.

On account of the increasing demand, and the difficulty in finding a suitable substitute, platinum is now worth $44.50 (1913) per ounce troy (31.02 g.), or double the value of gold ($20.67 per ounce).

675. Exercises.

1. Make an equation for: (a) the action of concentrated sulphuric acid on silver; (b) the decomposition of silver chloride by light.

2. Make an equation for: (a) the displacement of gold from potassium chloraurate by silver; (b) the decomposition of chloroplatinic acid, and of (c) ammonium chloroplatinate by heat; (d) the action of zinc on chloroplatinic acid.

3. What would be the advantages and disadvantages of using gold instead of platinum for crucibles?

CHAPTER XLI.

MANGANESE, CHROMIUM, AND RADIUM.

676. The first metallic elements we considered form simple positive ions (*e.g.* Na^+, Ca^{++}) only. The last two, on the other hand, appear almost exclusively in complex, negative ions, just as do the non-metallic elements ($AuCl_4^-$, $Au(CN)_2^-$, $PtCl_6^=$). Some of the intermediate metals can give negative ions (*e.g.* $ZnO_2^=$, $AlO_3^{=-}$), although in most of their compounds they are positive (Zn^{++}, Al^{+++}). The first two in the present chapter are equally familiar in *both* rôles.

MANGANESE Mn.

677. Ore and Preparation. The commonest ore of manganese is **pyrolusite** MnO_2, a soft, black mineral. The metal is obtained in pure form by mixing the pulverized dioxide with aluminium (Goldschmidt's process, p. 339) in a clay crucible and starting the reaction with magnesium:

$$3MnO_2 + 4Al \rightarrow 3Mn + 2Al_2O_3.$$

At the high temperature (over 3000°) the molten manganese sinks to the bottom, and the alumina floats above it.

678. Properties and Uses. Manganese is *hard* and crystalline, with a greyish-white *luster*. It is tarnished superficially by moist *air*. In fine powder it slowly displaces hydrogen from boiling *water*. It acts vigorously on dilute hydrochloric and sulphuric *acids*, giving **manganous** salts:

$$Mn + 2HCl \rightarrow MnCl_2 + H_2 \uparrow$$

The preparation and uses of spiegeleisen and ferro-manganese (p. 366), and of manganese steel (p. 372) have already been described. Traces of manganese seem to be essential to the growth of plants.

679. Manganous and Manganic Salts. There is a complete series of manganous salts ($MnCl_2$, $MnSO_4$, $MnCO_3$, etc.), in which the element forms the positive radical and is bivalent. They are all more or less distinctly *pink* in color.

With the borax bead all manganese compounds give an amethyst color (**manganic borate,** Mn^{III}) in the oxidizing flame, and a colorless bead (**manganous borate**) in the reducing flame.

680. Manganese Dioxide MnO_2. This oxide, composing the soft, black mineral **pyrolusite,** is the commercial source of the metal. It is an oxidizing agent, and is mixed with black paints to make them "dry" (p. 386) rapidly. For the same reason, and because it is a conductor, it is used as a depolarizer in dry batteries and in the Leclanché cell. It is added to molten glass to remove the green color due to ferrous silicate (p. 274).

681. Potassium Manganate K_2MnO_4. When manganese dioxide is fused in a porcelain crucible (or on a platinum wire) with potassium hydroxide and potassium nitrate (to furnish oxygen), a *green* mass of **potassium manganate** is obtained:

$$2KOH + MnO_2 + (O) \rightarrow K_2MnO_4 + H_2O.$$

This salt is very soluble in water, and can be secured in *green* crystals only by enclosing the vessel containing the solution along with another containing a drying agent ($CaCl_2$ or H_2SO_4). In this salt (K_2O,MnO_3) the manganese is sexivalent, and the manganate radical $MnO_4^{=}$ is bivalent.

682. Potassium Permanganate $KMnO_4$. If the green solution of the manganate be diluted with water, it changes to a purple-red color, manganese dioxide is precipitated, and the clear liquid gives, on evaporation, crystals of **potassium permanganate**:

$$3K_2MnO_4 + 2H_2O \rightarrow 4KOH + 2KMnO_4 + MnO_2 \downarrow$$

This salt crystallizes in needles which have a deep purple color with a greenish luster by reflected light. In this salt (K_2O,Mn_2O_7), the manganese is heptavalent, and the radical MnO_4^- is univalent. The purple color of the solution is the color of the ion MnO_4^-, while the ion $MnO_4^=$ of the manganates is green.

The solution of potassium permanganate, especially when, by addition of an acid, permanganic acid $HMnO_4$ has been formed, is an active oxidizing agent. We employed it in oxidizing hydrochloric acid to make chlorine (p. 108). For the same reason a dilute solution of potassium permanganate is used as an antiseptic and disinfectant.

CHROMIUM Cr.

683. Ore and Preparation. The chief ore of chromium is **chromite** FeO,Cr_2O_3, imported from Asiatic Turkey and New Caledonia.

The metal is easily obtained, by reducing chromic oxide Cr_2O_3 with aluminium (Goldschmidt process, p. 339).

684. Properties. Chromium is a lustrous *crystalline* metal. It does not tarnish in *air*. It displaces hydrogen, however, from dilute *acids*, giving **chromous** salts $CrCl_2$, $CrSO_4$, etc. Chromium (3 per cent) gives a hard steel, and is often used with nickel (p. 372) in armor plate.

The strange *alloys* which, although composed entirely of active metals, are hardly affected even by boiling acids (including nitric acid), usually contain chromium (*e.g.* 60 per cent Cr, 36 per cent Fe, 4 per cent Mo, no C).

685. Potassium Chromate K_2CrO_4. Powdered chromite is roasted with potash and lime:

$$4FeO,Cr_2O_3 + 8K_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2 \uparrow$$

and the potassium chromate dissolved out of the residue. It is a yellow, soluble salt (the ion $CrO_4^{=}$ is yellow), with which insoluble chromates of other metals, such as lead chromate $PbCrO_4$ (p. 385), can be precipitated.

When the solution is acidified, it turns red, and **potassium dichromate** $K_2Cr_2O_7$ crystallizes on evaporation:

$$2K_2CrO_4 + H_2SO_4 \rightarrow K_2SO_4 + 2KHCrO_4 \rightarrow K_2Cr_2O_7 + H_2O.$$

686. Potassium Dichromate $K_2Cr_2O_7$. This salt (see above), forms large orange-red crystals. It is related to the chromate (K_2O,CrO_3) by containing a double proportion of the anhydride — $K_2O,2CrO_3$. Like the chromate, the dichromate gives, by precipitation, the insoluble chromates.

When potassium hydroxide is added slowly to potassium dichromate solution, until the red color has changed to yellow, potassium chromate is formed:

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O.$$

Potassium (or sodium) dichromate solution is employed, instead of tan-bark, in tanning kid and glove leathers. Its use reduces the time required from 8 or 10 months to a few hours. A reducing agent is employed to precipitate **chromic hydroxide** $Cr(OH)_3$ (§§ 688, 689) in the leather.

By addition of sulphuric acid to a concentrated solution of a dichromate, **chromic anhydride** CrO_3 is precipitated in red crystals.

687. Classes of Chromium Compounds. It will be noted that three classes of compounds have been illustrated:

Chromous salts	$CrCl_2$, $CrSO_4$.	Cr bivalent.
Chromic compounds	$Cr(OH)_3$ and salts.	Cr trivalent.
Chromates	K_2CrO_4, $K_2Cr_2O_7$ (and CrO_3).	Cr sexivalent.

688. Chromic Sulphate $Cr_2(SO_4)_3$: Chrome-Alum. The chromic salts are made by *reduction* from chromates or dichromates. If potassium dichromate solution be acidified with sulphuric acid, only dichromic acid $H_2Cr_2O_7$ is formed. But if a reducing agent, like sulphurous acid, is added, then chromic sulphate is formed:

$$\begin{array}{l} \text{Partial (1): } K_2Cr_2O_7 + H_2SO_4 \rightarrow H_2Cr_2O_7 + K_2SO_4. \\ \text{Partial (2): } H_2Cr_2O_7 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 4H_2O + (3O). \\ \text{Partial (3): } \quad (3O) + 3H_2SO_3 \rightarrow 3H_2SO_4. \\ \hline K_2Cr_2O_7 + H_2SO_4 + 3H_2SO_3 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O. \end{array}$$

Adding the three partial equations, and cancelling $3H_2SO_4$ from each side, we get the final equation. When the solution stands, *purple* octahedral crystals of **chrome-alum** $K_2SO_4,Cr_2(SO_4)_3,24H_2O$ are formed (see p. 342). In photography this salt is often added to the fixing bath.

689. Chromic Hydroxide $Cr(OH)_3$ and Oxide Cr_2O_3. When an alkali is added to chrome-alum solution, chromic hydroxide $Cr(OH)_3$ (green) is precipitated:

$$Cr_2(SO_4)_3 + 6NaOH \rightarrow 2Cr(OH)_3 \downarrow + 3Na_2SO_4.$$

Chromic hydroxide is the substance precipitated in the leather (§ 686). It is used also as a mordant in calico printing and in wool dyeing. When the hydroxide is heated, **chromic oxide** Cr_2O_3 remains as a green powder.

Chromium compounds give with borax a *green* bead, containing **chromic borate.**

RADIUM Ra.

690. The Discovery of Radium. In 1896 Henri Becquerel discovered that a crystal of a salt of uranium could, in the dark, reduce the silver bromide on a photographic plate, even when a sheet of black paper (impervious to light) was placed between. Evidently a *radiation*, different from light, was given out by the salt. Next he discovered that an electrometer (Fig. 97), in which the gold leaves had been caused to separate by charging with electricity, lost its charge rapidly when a salt of uranium was brought near to the knob connected with the leaves. Evidently the salt *rendered the air a conductor*, and this permitted the escape of the electricity. These discoveries, in the hands of a multitude of observers, have led to the development of an entirely new branch of our science, namely **radio-chemistry.**

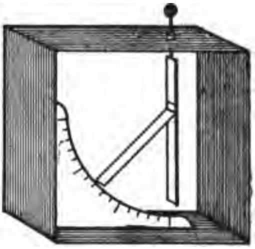


Fig. 97

Pierre Curie and Mme. Curie (née Marie Sklodovska) found that the mineral pitch blende, impure uranium oxide U_3O_8, had about four times the discharging speed of the pure salts. With prodigious labor the active element was extracted, in the form of the bromide, from pitch blende, and was named radium. The ore contains only 1 gram of radium per 3 tons.

691. Properties of Radium and its Salts. The metal (at. wt. 226) is white, and turns black in the air. It is bivalent ($RaBr_2$, $RaCl_2$, etc.), and belongs to the calcium family. The metal and its salts show one million times the radioactivity (discharging speed) of uranium. The radiations from the salts turn oxygen into ozone, char paper, and slowly disintegrate vessels of glass and quartz. The salts give off heat spontaneously at such a rate that 1 gram of the salt would raise a little over 1 gram of water per hour from 0° to 100°. The total heat available is calculated to be two thousand million calories per gram, or 250,000 times that obtainable by burning 1 gram of carbon.

692. The Nature of the Radiations. The radiations consist of electrically charged bodies, which "ionize" the air as they shoot through it, and so render it a conductor. When a particle of a radium compound is placed in air saturated with moisture, the ionized air, cooled by expansion (p. 196), condenses the moisture to fog. Thus the track of each emitted body appears as a line of fog, and the result is a tangled mass of fog-tracks which can be observed and photographed (Wilson).

There are *two* kinds of bodies emitted, namely positively charged atoms of the gas **helium** (p. 198), and particles of negative electricity called **electrons** (p. 145).

The atoms of **helium** (at. wt. 4) shoot out in almost straight lines with a speed of about 30,000 kilometers per second, going about 3.3 cm. in air, and ploughing their way right *through* air-molecules by the tens of thousands before being stopped, or even diverted from a straight path.

The **electrons** have a mass about $\frac{1}{1700}$ of that of a molecule of hydrogen. Being so light, their paths, straight at first, soon become tortuous, owing to collisions with the relatively very heavy air-molecules. The speed at first often approximates that of light (300,000 kilometers per sec.).

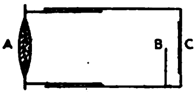
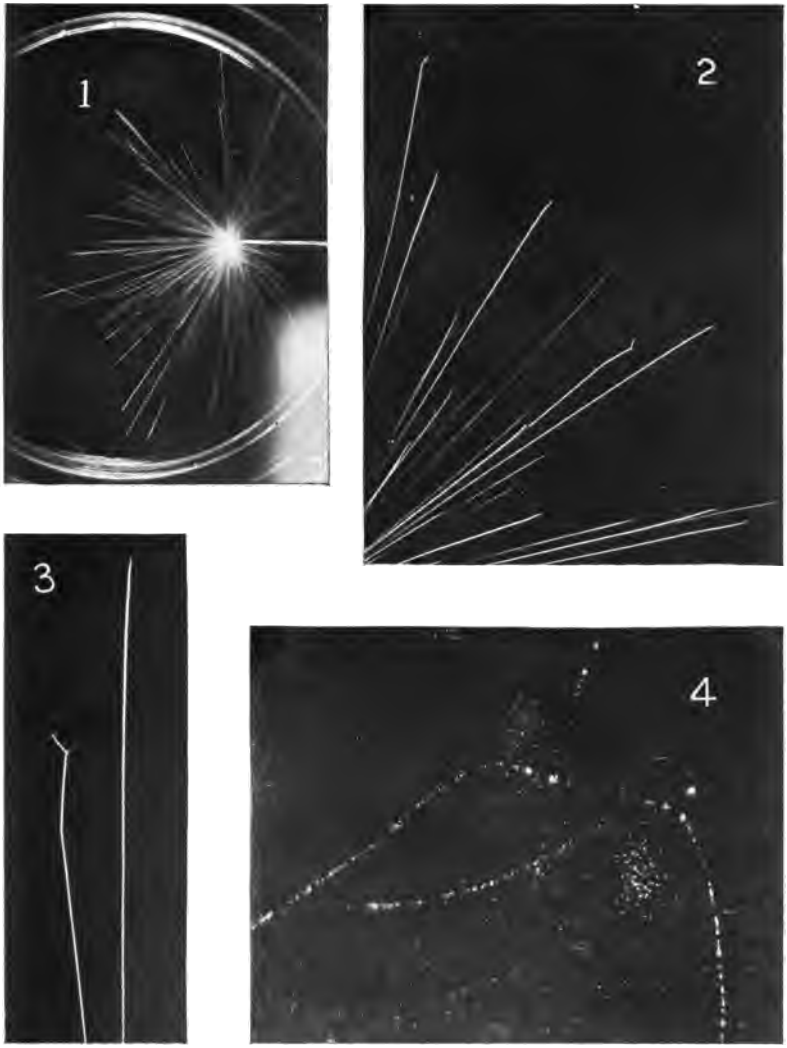


Fig. 98

The helium atoms can be detected also by means of Sir William Crookes' **spintharoscope** (Fig. 98). The surface *C* is covered with zinc blende, and some of the helium atoms from the radium bromide (at *B*) strike this surface and produce faint flashes of light. These are magnified by the lens



FOG-TRACKS FROM RADIUM (C. T. R. WILSON)

1, 2. Paths of helium atoms. 3. Part of 2, enlarged. 4. Paths of electrons.

A, and can be seen in a dark room after the eye has become thoroughly rested (15 to 20 minutes).

693. The Chemistry of Radioactivity. Patient chemical study of the phenomenon has shown the nature of the changes taking place. The radium atoms are *disintegrating*. Each gives an atom of helium (at. wt. 4), and an atom of a monatomic gaseous element, **niton** (Nt, p. 198). The weight of the atom of this gas (Ramsay) is 222.4 (which agrees with $226.4 - 4$). The gas has been liquefied (b.-p. $-153°$). Niton is chemically inert — that is it does *not combine* with other elements. It disintegrates rapidly, however, and in 4 days half of it has changed. Each atom loses another atom of helium and gives a radioactive solid, radium-A. This, in turn, is half gone in 4.3 minutes, giving an atom of helium and a solid, radium-B. The latter gives an electron (ϵ) from each atom and turns into radium-C. After several further steps, which, with those described, involve altogether the loss of 5 atoms of helium and at least 5 electrons ($5\ \epsilon$) per atom, a non-radioactive substance remains. Since the combined weight of the helium is $5 \times 4 = 20$, and $226 - 20 = 206$, this final product is supposed to be lead (at. wt. 207.1).

$$\begin{gathered}\mathrm{Ra} \rightarrow \mathrm{He} + \mathrm{Nt} \rightarrow \mathrm{He} + \mathrm{A} \rightarrow \mathrm{He} + \mathrm{B} \rightarrow \epsilon + \mathrm{C_1} \rightarrow \mathrm{He} + \\ \epsilon + \mathrm{C_2} \rightarrow \epsilon + \mathrm{D} \rightarrow \epsilon + \mathrm{E} \rightarrow \epsilon + \mathrm{F} \rightarrow \mathrm{He} + \mathrm{Pb}\ (?).\end{gathered}$$

The complex radioactivity of radium is due, therefore, to the presence with it of various amounts of *all* these products of its disintegration.

694. Radioactive Change. These radioactive changes differ markedly from all the chemical changes we have hitherto discussed. We can decompose a compound, or not, as we like. *These* changes take place *of their own accord* — we can neither start them nor stop them. Heating greatly hastens all ordinary chemical changes. These changes proceed at the *same rate* at 2000° as at −200°. Other chemical changes take place between atoms, these *within* the atoms.

695. Why do Radium and Uranium Always Occur Together? Investigation shows that uranium, after the radium has been removed, is still feebly radioactive. After a few months it recovers its full activity. Radium can be obtained from it an indefinite number of times. Evidently the uranium atom (at. wt. 238.5) itself disintegrates, losing, by stages which have been studied, three atoms of helium and giving radium (226.4).

696. Significance of Radioactivity. Uranium and thorium (also radioactive) are the elements with the highest known atomic weights. We can only imagine that these are survivors, other elements with still higher atomic weights having become extinct by disintegration. Perhaps the inactive elements now existing are simply the products of the disintegration of many radioactive elements of which the earth was once composed.

One interesting fact emerges from the study of radioactivity. The Brownian movement (p. 305) has revealed to us bodies of molecular dimensions, actually behaving exactly like the molecules of which we had imagined matter to be composed. The study of this movement by Perrin, a French chemist, has provided us with several ways of estimating the actual weights of molecules. Now, the sensitive electroscope enables us actually to count single, charged atoms of helium as they enter the instrument, and the fog-tracks enable us to follow their movements. The molecules and atoms of our hypotheses have thus been shown to be literal facts.

Another interesting by-product of this subject is the calculation that the heat given off by the disintegration of the radium known to exist in the earth (niton is found in the soil and in well waters) is sufficient *alone* amply to account for the maintenance of its temperature. A globe the size of the earth, possessing originally only heat energy, and cooling from a white-hot condition to the temperature of interstellar space, would have passed through the stage of habitable temperatures in a much shorter time than that which geological deposits and fossils show to have been actually available. The discovery of the enormous, but gradually released, disintegration energy of radium, enables us now to explain the prolonged period during which life has existed in the earth.

697. Exercises.

1. Give a list of the classes of manganese compounds and, in each class, the formulæ of several compounds, the prevailing color, and the valence of manganese in that class.

2. Make equations for the formation of: (a) manganous sulphate; (b) manganous carbonate (insol.); (c) sodium manganate; (d) the oxidation of hydrochloric acid by potassium permanganate.

3. What action did we find to be catalyzed by manganese dioxide?

4. In what respects are uranium and radium like, and in what respects unlike ordinary chemical compounds?

CHAPTER XLII.

THE RECOGNITION OF SUBSTANCES, II — A REVIEW OF THE METALLIC ELEMENTS.

698. As in Chapter XXX, so here, we assume that the specimen to be identified contains a single substance. We consider now the metallic elements, and limit ourselves to the twenty-one that have been described in the context. Our review will cover, mainly, the metallurgy and some of the physical properties of each metal.

Although arsenic has been stated to be a non-metallic element, and antimony to be partially non-metallic, it is more convenient in problems of recognition to classify them with the metallic elements. They are therefore included in the twenty-one.

699. External Examination. The COLOR is often significant. Most of the common compounds of iron, nickel, cobalt, copper, gold, manganese and chromium are colored (see text). A METALLIC LUSTER (scrape off the tarnish) usually, though not always, indicates a free metal or an alloy. The CRYSTALLINE FORM should be noted. The ODOR usually gives information about non-metallic constituents (p. 292) only. As regards STATE, the vast majority of the metals and their compounds are **solids**. A few are liquids (*e.g.* Hg and $Ni(CO)_4$, p. 380) or gases. When a **liquid** presents itself, therefore, it is usually an aqueous solution of some compound. Obtain the solid by evaporation.

700. Solubility and Reaction of the Solution. Ascertain whether the substance is SOLUBLE in water (p. 290). Note whether the solution is ACID, ALKALINE, or NEUTRAL in reaction (p. 282). No substance can be identified by the preceding observations alone, but the final conclusion as to the nature of the specimen must be in harmony with them.

701. The Match Test (Solids).* This experiment results, in many instances, in the liberation of the metal by a metallurgical reaction. We are thus able to recognize it, largely by its physical properties.

A match-stick is rubbed with a warmed (and partly melted) crystal of washing soda, and is then charred in the Bunsen flame. A few particles each of the specimen and of dry sodium carbonate are made into a paste with part of a drop of water. The small mass is then stuck on the end of the match, and held in the reducing region of a low Bunsen flame. The compound, whatever it may be, interacts with the sodium carbonate, giving first the carbonate and then the oxide of the metal. The oxide (*if reducible*) is reduced by the carbon, and the metal liberated. The end of the match is then ground in a mortar under water, and the charcoal and soda washed away. Shining or heavy grey particles indicate a metal.

702. Results of the Match Test. The following metals, although liberated, are VOLATILE, and are *not* found in the match test, namely: arsenic, antimony, bismuth, zinc, and mercury (see, therefore, § 703).

Some metals, since their oxides are NOT REDUCIBLE by carbon in the Bunsen flame, namely calcium, magnesium, aluminium, manganese, and chromium, give *no* metal (see, therefore, § 704).

Compounds of potassium and sodium are reduced with difficulty by carbon, and in any case the metals are volatile,

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* Many experimental details, essential for the successful performance of the tests described in this chapter, are here omitted. They will be found in the Author's *Laboratory Outline of Elementary Chemistry*.

so that these metals also give no result (see § 704). Of the twenty-one metals *nine* can be *found* by the match test:

Six of these metals are MALLEABLE and give SHINING PARTICLES. **Yellow** particles are *gold* or *copper*. The particles are transferred on the point of a knife blade to a piece of filter paper, treated with a drop of nitric acid, and warmed gently. Copper dissolves leaving a green stain. Gold will not dissolve until a drop of hydrochloric acid also (making *aqua regia*) is added.

Silver white particles may be silver, lead, tin, or platinum. Place the particles in a watch glass, add nitric acid and warm. *Silver* dissolves, and the solution gives a white precipitate (AgCl) with hydrochloric acid (p. 400). *Lead* also dissolves, gives however no precipitate (p. 385, solution too dilute) with hydrochloric acid, but does give one with sulphuric acid (p. 385). Tin interacts with nitric acid, to give a white, insoluble substance (p. 387). *Platinum* is insoluble in nitric acid, but dissolves upon addition of hydrochloric acid (*aqua regia*).

Three metals give HEAVY GREY particles, namely, iron, cobalt, and nickel. A **magnetized** knife blade attracts *iron* particles powerfully — the others rather feebly. The particles, transferred to a piece of filter paper and touched with concentrated hydrochloric acid, dissolve and, after warming, give a *yellow* stain (iron) or a *blue* stain (*cobalt*). A drop of nitric acid and warming give a greenish stain (*nickel*). Confirm these three by **borax bead** tests (pp. 379, 380, and 381).

703. Recognition of Compounds of the Volatile Metals: Film Tests. In case of a negative result with the match test, the specimen may be a compound of one of the volatile metals (§ 702), arsenic, antimony, bismuth, mercury, or zinc. A particle of the compound is placed on the moistened end of a stiff fiber of asbestos and is held in the tip of the reducing part of a low Bunsen flame. The latter contains hydrocarbons and free hydrogen, which liberate the metal.

A porcelain dish, held close above the end of the fiber, will condense the vapor of the metal. A scattered DUST is *mercury*. A continuous BLACK METALLIC FILM is arsenic, antimony, bismuth, or zinc. Lead, if missed in the match test, being somewhat volatile, will be found here also. **Dilute nitric acid** dropped on the film dissolves *zinc* and *lead* instantly, the other metals slowly (Bi) or practically not at all (As, Sb).

When the experiment is repeated, with the porcelain dish held high up in the flame, the vapor of the metal (except mercury) is oxidized and the OXIDE is deposited on the dish. A **yellow** deposit is *bismuth* trioxide (or, if faint, PbO). The oxides of arsenic, antimony, and zinc are white and invisible. They may be distinguished, however, by blowing HYDROGEN IODIDE over the dish to produce the iodides: **yellow** is *arsenic* (AsI_3), **orange** is *antimony* (SbI_3), **colorless** (invisible) is *zinc* (ZnI_2). Bismuth (already identified) gives by this test a bluish-brown to red color (BiI_3) and lead (already identified, § 702) a yellow (PbI_2). The last can be recognized because it is insoluble in water (p. 385) and therefore is not affected by breathing on the dish, while the other iodides are soluble and disappear (dissolve, to reappear on drying).

704. Recognition of Metals whose Oxides are not Reduced. There remain seven metals whose compounds give a negative result in the match and film tests. In case of such a negative result, the substance may be heated on a platinum wire in the Bunsen flame for the FLAME TEST. A **brick-red** color indicates a compound of *calcium;* a **reddish-violet,** *potassium;* a very strong **yellow,** *sodium.*

The BORAX BEAD test gives an **amethyst** color with compounds of *manganese* and a **green** with those of *chromium.*

A small scrap of filter paper, in which a few particles of the substance have been wrapped, is held by a platinum wire twisted (two or three turns) round it. The ball is charred in the Bunsen flame and is then moistened with a drop of a dilute solution of a SALT OF COBALT, and is heated once more. A **blue** color (p. 341) indicates a compound of *aluminium* (a green, a compound of *zinc*, p. 335).

Compounds of the only remaining metal, *magnesium*, give an indefinite color (more or less pink) by the foregoing test. In case all the preceding tests have given negative results, add to a solution of the substance (1 c.c.) a few drops each of solutions of ammonium chloride, ammonium hydroxide, and sodium-hydrogen phosphate Na_2HPO_4. A **white, crystalline precipitate** (NH_4MgPO_4) indicates a compound of *magnesium*.

705. Recognition by Reactions in Solution. Starting with the substance in solution, its identity can also be ascertained by using reactions involving mainly precipitations and oxidations or reductions. This method is of especial value when the material contains more than one substance.

For example, when HYDROCHLORIC ACID is added to the solution, a **white precipitate** ($AgCl$, $HgCl$, or $PbCl_2$) indicates the presence of *silver-ion*, *mercurous-ion*, or *lead-ion*. The other metal-ions are not precipitated, and may be separated from those three by filtration. These three chlorides can be distinguished from one another very easily. When ammonium hydroxide is added to the precipitate, silver chloride dissolves (§ 667), mercurous chloride turns black (p. 396), and lead chloride remains apparently unchanged ($Pb(OH)_2$).

A definite plan of procedure enables us systematically to separate and identify every one of the positive ions. To give, *and explain*, the scheme in its entirety, however, would compel us to apply, and to apply rigorously and quantitatively, principles which we have touched upon, but not fully developed. Analytical chemistry is too complex a subject for brief treatment, but fascinating in the extreme when once it has been mastered.

706. Exercises.

1. Name some substances that have a metallic luster, but are not metals or alloys.

2. Name the metals whose salts with active acids will give: (a) neutral aqueous solutions; (b) acid aqueous solutions. What classes of salts will give alkaline solutions?

3. Show by what three successive changes (give equations) cupric sulphate would be acted upon in the match test (§ 701), so as finally to leave copper.

4. Give two distinctive reactions by which the green stain (§ 702) could be shown to be a salt of copper.

5. What is the action of nitric acid on tin?

6. What results do the borax bead tests give with compounds of iron, cobalt, and nickel?

7. Make equations for the action of hydrogen (§ 703) on: (a) arsenic trioxide: (b) antimony trichloride; (c) bismuth trichloride.

8. Make equations for the oxidation of: (a) arsenic; (b) antimony; (c) bismuth.

9. Make equations for the action of hydrogen iodide on the oxides of: (a) arsenic; (b) antimony; (c) zinc.

10. What are the interactions of a salt of cobalt heated (dry) with a compound of: (a) aluminium; (b) zinc?

11. Make an equation for the interaction of ammonium hydroxide, magnesium sulphate, and sodium phosphate.

12. Make equations for the actions of ammonium hydroxide solution on chlorides of: (a) silver-ion; (b) mercurous-ion; (c) lead-ion.

APPENDIX.

I. The Metric System.

Length. 1 meter = 10 decimeters = 100 centimeters (100 cm.) = 1000 millimeters (1000 mm.).

1 decimeter = 10 centimeters = nearly 4 inches.

Volume. 1 liter = 1000 cubic centimeters (1000 c.c.) = a cube 10 cm. × 10 cm. × 10 cm.

1 liter = 1.057 quarts (U.S.) or 1.136 quarts (Brit.).
1 fl. ounce (U.S.) = 29.57 c.c. 1 ounce (Brit.) = 28.4 c.c.

Weight. 1 gram (g.) = wt. of 1 c.c. of water at 4° C. 1 kilogram = 1000 g.

1 kilogram = 2.2 lbs. avoird. (U.S. and Brit.).
1 ounce avoird. (U.S. and Brit.) = 28.35 g.
1 nickel (U.S.) weighs 5 g. 1 halfpenny (Brit.) weighs 5 to 5.7 g.

II. Scale of Hardness.

Each of the following minerals will scratch the surface of a specimen of any one *preceding* it in the list.

1. Talc
2. Gypsum (or NaCl)
3. Calcite (or Cu)
4. Fluorite
5. Apatite
6. Felspar
7. Quartz
8. Topaz
9. Corundum
10. Diamond

Glass is slightly scratched by 5, and easily by those following. Glass will not scratch 5 distinctly, but will scratch those preceding 5.

A good **knife** scratches 6 slightly, but not those following.

A **file** will scratch 7, but not those following.

III. Temperatures Centigrade and Fahrenheit.

Upon the centigrade scale, the freezing-point of water is 0° C. and the boiling-point 100° C. Upon the Fahrenheit scale, the same points are 32° F. and 212° F., respectively. The same interval is thus 100° on the one scale and 180° on the other. The degree Fahrenheit is therefore $\frac{100}{180}$ or $\frac{5}{9}$ of 1° Centigrade. Any temperatures can be converted by using the formulæ:

$$\text{C.}^\circ = \frac{5}{9}\,(\text{F.}^\circ - 32), \qquad \text{F.}^\circ = \frac{9}{5}\,(\text{C.}^\circ) + 32.$$

The following table (IV) contains the temperatures from 0° C. to 35° C., with the corresponding values on the Fahrenheit scale (32° F. to 95° F.).

IV. Vapor Pressures of Water.

Both the Fahrenheit (F.) or ordinary and the Centigrade (C.) temperatures are given.

Temperature.		Pressure, mm.	Temperature.		Pressure, mm.
F.	C.		F.	C.	
32°	0°	4.6	71.6°	22°	19.7
41	5	6.5	73.4	23	20.9
46.4	8	8.0	75.2	24	22.2
48.2	9	8.6	77.0	25	23.6
50.0	10	9.2	78.8	26	25.1
51.8	11	9.8	80.6	27	26.5
53.6	12	10.5	82.4	28	28.1
55.4	13	11.2	84.2	29	29.8
57.2	14	11.9	86.0	30	31.5
59.0	15	12.7	87.8	31	33.4
60.8	16	13.5	89.6	32	35.4
62.6	17	14.4	91.4	33	37.4
64.4	18	15.4	93.2	34	39.6
66.2	19	16.3	95.0	35	41.8
68.0	20	17.4			
69.8	21	18.5	212.0	100	760.0

V. Order of Activity of the Metals.

Each metal, when placed in a solution of a salt of one of the metals *following* it in the list, displaces the second metal and deposits it in the free condition (see pp. 42, 393, 397, 399).

Potassium
Sodium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Chromium
Iron
Nickel
Tin
Lead
Hydrogen
Copper
Bismuth
Antimony
Mercury
Silver
Platinum
Gold

INDEX

⁂ The numbers refer to pages.

Monel metal resists Chem action
used for valve seats use gate valve

TABLE OF THE PERIODIC SYSTEM.

The highest **valences** towards hydrogen and oxygen are shown in the top line (E = element).

The members of the same **family** of elements (§ 400) are arranged vertically. There are two families in each column, one on the left and one on the right.

E^0	$E^{I}Cl$ $E_2^{I}O$	$E^{II}Cl_2$ $E^{II}O$	$E^{III}Cl_3$ $E_2^{III}O_3$	$E^{IV}H_4$ $E^{IV}O_2$	$E^{III}H_3$ $E_2^{V}O_5$	$E^{II}H_2$ $E^{VI}O_3$	EH $E_2^{VII}O_7$	$E^{VIII}O_4$.
He, 4 Ne, 20	Li, 7 Na, 23	Gl, 9 Mg, 24.3	B, 11 Al, 27	C, 12 Si, 28	N, 14 P, 31	O, 16 S, 32	F, 19 Cl, 35.5	. . . .
A, 39.9	K, 39 Cu, 63.6	Ca, 40 Zn, 65.4	Sc, 44 Ga, 70	Ti, 48 Ge, 72.5	V, 51 As, 75	Cr, 52 Se, 79.2	Mn, 55 Br, 80	Fe, 56 Co, 59 Ni, 58.7
Kr, 83	Rb, 85.4 Ag, 108	Sr, 87.6 Cd, 112.4	Y, 89 In, 115	Zr, 90.6 Sn, 119	Cb, 93.5 Sb, 120	Mo, 96 Te, 127.5	. . . I, 127	Ru, 102 Rh, 103 Pd, 107
Xe, 130	Cs, 133 Au, 197	Ba, 137.4 Hg, 200.6	La, 139 Tl, 204	Ce, 140 Pb, 207	Ta, 181.5 Bi, 208	W, 184 . . .	. . . . . .	Os, 191 Ir, 193 Pt, 195
Nt, 222.5	. . .	Ra, 226.5	. . .	Th, 232.5	. . .	U, 238.5	. . .	. . . .

INTERNATIONAL ATOMIC WEIGHTS (1917)

		O = 16.
Aluminium	Al	27.1
Antimony	Sb	120.2
Argon	A	39.88
Arsenic	As	74.96
Barium	Ba	137.37
Bismuth	Bi	208.0
Boron	B	11.0
Bromine	Br	79.92
Cadmium	Cd	112.40
Caesium	Cs	132.81
Calcium	Ca	40.07
Carbon	C	12.005
Cerium	Ce	140.25
Chlorine	Cl ✓	35.46
Chromium	Cr	52.0
Cobalt	Co	58.97
Columbium	Cb	93.1
Copper	Cu	63.57
Dysprosium	Dy	162.5
Erbium	Er	167.7
Europium	Eu	152.0
Fluorine	F	19.0
Gadolinium	Gd	157.3
Gallium	Ga	69.9
Germanium	Ge	72.5
Glucinum	Gl	9.1
Gold	Au	197.2
Helium	He	4.00
Holmium	Ho	163.5
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.92
Iridium	Ir	193.1
Iron	Fe	55.84
Krypton	Kr	82.92
Lanthanum	La	139.0
Lead	Pb	207.20
Lithium	Li	6.94
Lutecium	Lu	175.0
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.6
Molybdenum	Mo	96.0
Neodymium	Nd	144.3
Neon	Ne	20.2
Nickel	Ni	58.68
Niton (radium emanation)	Nt	222.4
Nitrogen	N ✓	14.01
Osmium	Os	190.9
Oxygen	O	16.00
Palladium	Pd	106.7
Phosphorus	P ✓	31.04
Platinum	Pt	195.2
Potassium	K	39.10
Praseodymium	Pr	140.9
Radium	Ra	226.0
Rhodium	Rh	102.9
Rubidium	Rb	85.45
Ruthenium	Ru	101.7
Samarium	Sa	150.4
Scandium	Sc	44.1
Selenium	Se	79.2
Silicon	Si	28.3
Silver	Ag	107.88
Sodium	Na	23.00
Strontium	Sr	87.63
Sulphur	S ✓	32.06
Tantalum	Ta	181.5
Tellurium	Te	127.5
Terbium	Tb	159.2
Thallium	Tl	204.0
Thorium	Th	232.4
Thulium	Tm	168.5
Tin	Sn	118.7
Titanium	Ti	48.1
Tungsten	W	184.0
Uranium	U	238.2
Vanadium	V	51.0
Xenon	Xe	130.2
Ytterbium (Neoytterbium)	Yb	173.5
Yttrium	Yt	88.7
Zinc	Zn	65.37
Zirconium	Zr	90.6